**Editor Decision: Publish subject to minor revisions (review by Editor)** (12 Oct 2016) by Dr Kumiko Goto-Azuma

Comments to the Author:

1. Section 2.1 and Fig. 3.

22 cm water eq and 12 months resolution, makes each month less than 2 cm. Is this really resolved all the way in the record at Summit (Fig 3)?

Yes, we typically achieved sub 1 cm resolution. Which means at least one data point per month.

How come there is a shift between the two time periods in Na, if Na is the main parameter used to make the annual layer counting?

The minimum in the ratio of S/Na is the parameter that is used to define the annual layer boundaries, so any shift in the pure Na signal must be compensated by shift in S in the opposite direction. Pure Na, Ca and  $H_2O_2$  signals maxima were identified in order to confirm the identification of an annual cycle.

2. To me, lines 532-535 (P. 22) seem to contradict with lines 540-542. Please clarify the logic.

I think the Editor is referring to lines 632 and 640 of page 22(?) As I can see there is an apparent contradiction between the two statements. It is very clear from the high resolution comparison between the Br and S records that there is no immediate response to the volcanic eruptions reflected in the bromine record. So I don't think that the second statement on line 640 is dispute. The earlier statement made a suggestion that the atmospheric sulfur may influence the nsiBr record and could be the cause of the negative values because there was some coarse overlap in the timing of volcanic activity and industrial activity and the negative nsiBr values. This is a weakly surmised conclusion, (and as noted by the Editor, is in contradiction to the later statement) it was purely speculative – there are many things that happen coincidently with broad periods of negative nsiBr values, it was merely an observation that sulfur increases were one such factor – so to avoid confusion the statement has been removed from the manuscript.

3. The caption of Fig. 6 (line 1073).

3-1. There seems to be no red curve in Fig.6. There are thin and thick orange curves instead.

The line has been made thicker and a brighter red. Caption updated

3-2. The legend for the thin orange curve reads "MSA no volc". Isn't this "MSA, outliers removed"? These mean the same thing but to be consistent the legend wording was changed to "outliers rem." Also the lines were labelled incorrectly. The red one is the raw MSA and the orange one "outlier rem."

4. Same comments for Fig. 7 caption.
updated as above
5. The last line of the Fig. S9 caption.
The longitude seems to be wrong. It should be same as that for (a).
Corrected thanks.

- 1 Sea ice and pollution-modulated changes in Greenland ice core
- 2 methanesulfonate and bromine
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- 11 Keywords: bromine, MSA, nitrate, sea ice, pollution, acidification, Arctic, Greenland, cryosphere

# 13 Abstract

14 Reconstruction of past changes in Arctic sea ice extent may be critical for understanding its future 15 evolution. Methanesulphonate (MSA) and bromine concentrations preserved in ice cores have both been proposed as indicators of past sea ice conditions. In this study, two ice cores from central and NE 16 17 Greenland were analysed at sub-annual resolution for MSA  $(CH_3SO_3H)$  and bromine, covering the time 18 period 1750-2010. We examine correlations between ice core MSA and the HadISST1 ICE sea ice 19 dataset and consult back-trajectories to infer the likely source regions. A strong correlation between the 20 low frequency MSA and bromine records during preindustrial times indicates that both chemical species 21 are likely linked to processes occurring on or near sea ice in the same source regions. The positive 22 correlation between ice core MSA and bromine persists until the mid-20th century, when the acidity of 23 Greenland ice begins to increase markedly due to increased fossil fuel emissions. After that time, MSA 24 levels decrease as a result of declining sea ice extent but bromine levels increase. We consider several 25 possible explanations and ultimately suggest that increased acidity, specifically nitric acid, of snow on 26 sea ice stimulates the release of reactive Br from sea ice, resulting in increased transport and deposition 27 on the Greenland ice sheet.

# 29 1 Introduction

30 Atmospheric chemistry in the polar regions is strongly modulated by physical, chemical, and biological processes occurring in and around sea ice. These include sea salt aerosol generation, biogenic emissions 31 32 of sulfur-containing gases and halogenated organics, and the photochemical/heterogeneous reactions 33 leading to release of volatile, reactive bromine species. The resulting chemical signals influence the 34 chemistry of the aerosol deposited on polar ice sheets. For this reason ice core measurements of sea salt 35 ions, methanesulphonate (MSA), and bromine have been examined as potential tracers for sea ice extent 36 (Abram et al., 2013; Spolaor et al., 2013b, 2016; Wolff et al., 2003). The interpretation of such tracers 37 is complicated by the fact that their source functions reflect changes in highly complex systems, and 38 signals are further modified by patterns of atmospheric transport and deposition.

39 MSA is produced by the atmospheric oxidation of DMS ( $(CH_3)_2S$ ). DMS is produced throughout the 40 world's oceans as a breakdown product of the algal metabolite DMSP,  $((CH_3)_2S^+CH_2CH_2COO^-)$ . DMS emissions are particularly strong in marginal sea ice zones (Sharma et al., 2012), and this source 41 42 is believed to be a dominant contributor to the MSA signal in polar ice (Curran and Jones, 2000). Ice 43 core MSA records have been used extensively in Antarctica as a proxy for local sea ice dynamics. Although the specifics of the relationship are highly site-dependent (Abram et al., 2013; Curran et al., 44 45 2003) MSA has been proven to be a reasonably good proxy for sea ice conditions (e.g., (Curran and Jones, 2000)). In the Arctic, the relationship between MSA and sea ice conditions is less straightforward 46 47 due to the likelihood of multiple source regions with different sea ice conditions contributing to the ice 48 core archived MSA (Abram et al., 2013). Until now, a significant, (r =-0.66) relationship between ice 49 core MSA and Artic sea ice extent (specifically August in the Barents sea) has only been established 50 for a short record from a Svalbard ice core (O'Dwyer et al., 2000). In this study we analyse the direct 51 correlations between the MSA records from two Greenland ice core sites and the surrounding sea ice 52 conditions in order to demonstrate the utility of MSA as a local sea ice proxy.

In this study, all dissolved or suspended bromine species are measured (including organic bromine) and shall be referred to as "bromine". The primary source of total inorganic bromine (e.g.  $Br_2, Br^-, HBr$ ) in the marine boundary layer (MBL) is the ocean (Parrella et al., 2012; Sander et al., 2003). At concentrations of less than 0.2% that of sodium (Na), bromide ( $Br^-$ ) makes a small contribution to ocean salinity.  $Br^-$  can be concentrated in the high latitude oceans when the sea water is frozen, since the formation of the ice matrix exudes the sea-salts in the form of brine (Abbatt et al., 2012). Small, seasalt aerosol particles blown from the surface of sea ice are typically enriched with bromine (Sander et

60 al., 2003) and satellite imagery has revealed that plumes of bromine (as BrO) are photo-chemically released from sea-ice zones in spring (Nghiem et al., 2012; Schönhardt et al., 2012; Wagner et al., 2001). 61 62 Recently, studies have begun to link ice core records of bromide enrichment (relative to sea water Na 63 concentrations) preserved in polar ice sheets to that of local sea ice conditions (Spolaor et al., 2013a, 64 2013b, 2014). Spolaor and co-workers demonstrated the spring-time  $Br^{-}/Na$  that is preserved in the 65 ice core is a record of bromine explosion events over adjacent seasonal sea ice. A  $Br^{-}/Na$  enrichment would therefore indicate a larger seasonal sea ice extent or conversely a shorter distance between the 66 67 ice edge and the ice core site due to decreased multi-year sea ice (Spolaor et al., 2013a). However, like 68 MSA, it is likely that the bromine - sea-ice relationship in the Arctic is complicated by the myriad of 69 bromine source regions which influence an ice core record in addition to factors which influence the 70 degree of enrichment of the aerosol as it travels to the ice core site. In this study we compare ice core 71 records of bromine to those of MSA and other common MBL species in order to determine the influence 72 of sea ice conditions and other factors on bromine concentrations.

Here we present measurements of MSA, bromine, and elemental tracers of sea salt and crustal input in two Greenland ice cores covering the time period 1750-2010 C.E.. These ice core records represent the first continuous, sub-annual resolution records of bromine in polar ice to extend beyond the satellite era. We examine the relationship between these two sea ice-modulated tracers, their relationship to independent historical estimates of sea ice distribution, and the influence of industrialization on atmospheric and ice core chemistry.

# 79 2 Methods

#### 80 2.1 Ice cores

The 87 m 'Summit-2010' ice core was collected in 2010 close to Summit Station, Greenland (72°20'N 38°17'24"W, Fig. 1). The average snow accumulation at Summit, as determined from the ice core record, is ~0.22 m yr<sup>-1</sup> water equivalent, with few instances of melt. Due to the relatively high snow accumulation rate, seasonal analysis of the sea salt species concentrations was feasible. The 213 m Tunu core was collected in 2013 (78° 2' 5.5"N, 33° 52' 48"W, Fig. 1), approximately 3 km east of the Tunu-N automatic weather station, part of the Greenland Climate Network. The average snow accumulation at Tunu, as determined from the ice core record, is ~0.11 m yr<sup>-1</sup> water equivalent.

88 The Summit-2010 and Tunu cores were dated using volcanic horizons in sulfur (S) from well dated

89 historic eruptions (e.g., 1815, 1835, 1846, 1854, 1873, 1883, 1912). The dating of both cores was refined

90 by annual layer counting using seasonal cycles in Na, Ca, and the ratio of non-sea salt S/Na as described

in more detail for another Greenland ice core (NEEM-2011-S1) by Sigl et al., (2013, 2015). Annual-91 92 layer boundaries (nominal January) were defined as the minimum value in the ratio of non-sea salt S/Na 93 following Sigl et al. (2013). The seasonal cycles in Na and Ca (from sea-salt and mineral dust emissions 94 peaking in winter months) remain largely unaffected by rising anthropogenic emissions during the 95 industrial period and thus can be used for annual layer counting for the entire record. The minimum in 96 hydrogen peroxide was also used as a winter marker in the upper section of the Summit-2010 core. 97 Timing was evaluated for consistency against other parameters including insoluble particle counts and 98 black carbon. Monthly values were calculated assuming a constant distribution of snowfall within each 99 year. Because of the lower accumulation rate and strong katabatic winds at the Tunu site, constraints 100 from volcanic synchronization played a more important role in the developing the depth-age scale for 101 the Tunu core compared with Summit-2010. First the Tunu non-sea salt S record was synchronized to 102 the NEEM-2011-S1 volcanic record (Sigl et al., 2015) and then the required number of annual layers 103 between volcanic horizons picked from the high-resolution chemistry.

The annual-layer dating for these ice cores resulted in a plutonium record that is consistent with other ice cores from Greenland between 1950 and 1970 and with the emission histories from nuclear weapon testing in the Northern Hemisphere (Arienzo et al., 2016). The error in the dating of the ice core records was estimated as  $\pm 0.33$  years for the Summit-2010 record and  $\pm 1$  years for the Tunu record.

### 108 2.2 Sampling and analysis

109 The ice cores were sampled from 33x33 mm cross-section sticks using a continuous melter system 110 (McConnell et al., 2002). The silicon carbide melter plate provides three streams from concentric square regions of the ice core sample: an innermost stream (with a cross sectional area of 144 mm<sup>2</sup>), an 111 intermediate stream (340 mm<sup>2</sup>) and an outer stream that was discarded along with any contaminants 112 obtained from handling of the ice core. The innermost melt stream was directed to two inductively 113 114 coupled plasma-mass spectrometers (ICP-MS, Thermo Element II high resolution with PFA-ST 115 concentric Teflon nebulizer (ESI)) run in parallel. All calibrations and runtime standards were run on 116 both instruments and several elements were also measured in duplicate (Na, Ce, Pb) to ensure tracking 117 between both ICP-MS. In addition, an internal standard of yttrium flowed through the entire analytical 118 system and was used to observe any change in system sensitivity. The instrument measuring bromine 119 was run at medium resolution and there were no mass interferences observed at the bromine isotope mass monitored (79 amu). The sample stream was acidified to 1% HNO3 to prevent loss of less soluble 120 121 species, degassed just prior to analysis to minimize mixing in the sample line and sampled at a rate of 0.45ml min<sup>-1</sup> (McConnell et al., 2002; Sigl et al., 2013). The following elements were measured by 122

ICP-MS: Br, Cl, Na, Ca, S, Ce, and Pb. Calibration of the ICP-MS was based on a series of 7 mixed 123 standards measured at the start and end of each day for all elements except for the halides. Due to the 124 125 high volatility of acid halides, a set of 4 bromine and chlorine standards were made individually in a 1% UHP HNO<sub>3</sub> matrix from fresh, non-acidified intermediate stock solution (Inorganic Ventures) every 126 127 day. The intermediate melt stream was directed to a continuous flow analysis (CFA) system on which nitrate ion  $(NO_3^-)$  and snow acidity (sum of soluble acidic species) were measured using the technique 128 129 described by Pasteris (2012) in addition to other atmospheric species of interest (Röthlisberger et al., 130 2000). Stable water isotopes records were also collected using the CFA system according to the method described by Maselli et al. (2013) 131

The analysis of MSA by batch analysis using ESI/MS/MS has been reported previously (Saltzman et 132 al., 2006). A portion of the debubbled CFA melt stream (150 µl min<sup>-1</sup>) was subsampled for continuous 133 134 on-line analysis of methanesulfonate by electrospray triple-quad mass spectrometer (ESI/MS/MS; 135 Thermo-Finnigan Quantum). This subsample was mixed with pure methanol (50  $\mu$ l min<sup>-1</sup>) delivered 136 using an M6 pump (syringe-free liquid handling pump, VICI). The methanol was spiked with an 137 internal standard of deuterated MSA (CD<sub>3</sub>SO<sub>3</sub>; Cambridge Isotopes) at a concentration of 52 nM. The 138 internal isotope standard was used to correct for any changes in instrument response due to variations 139 in water chemistry (such as acidity). The isotope standard was calibrated against non-deuterated MSA 140 standards prepared in water from non-deuterated MSA (CH<sub>3</sub>SO<sub>3</sub>; Sigma Aldrich). MSA was detected in negative ion mode using the  $CH_3SO_3^-/SO_3^-$  transition (m/z 95/80) and  $CD_3SO_3^-/SO_3^-$  (m/z 98/80). The 141 concentration of MSA in the sample flow was determined from the ratio of the non-deuterated and 142 deuterated signals after minor blank corrections. This study is the first use of the technique for ice core 143 144 MSA analysis in a continuous, online mode. The uncertainty in the MSA intensity as calculated from 145 the standard calibrations is 1%.

A second portion of the debubbled CFA melt stream was directed to an autosampler collection systemto collect a discretely sampled archive of the melted ice cores. The collected samples were frozen at the

148 end of each day and later analysed for MSA again using ion chromatography and ESI/MS/MS.

# 149 2.3 Calculation of anthropogenic Pb, non sea-salt S, and Br enrichment

The Pb derived from anthropogenic sources (exPb) was calculated as the difference between total lead measure in the ice core,  $[Pb]_{obs}$ , and that from dust sources. The Pb from dust was calculated as a

152 fraction of the dust proxy cerium,  $([Ce]_{obs})$ .

154 
$$\mathbf{exPb} = [\mathbf{Pb}]_{obs} - [\mathbf{Ce}]_{obs} \times \left(\frac{[\mathbf{Pb}]}{[\mathbf{Ce}]}\right)_{dust}$$
153

Where the relative amount of Pb in dust, ([Pb]/[Ce])<sub>dust</sub>, has the constant mass ratio of 0.20588
(Bowen, 1979).

157 Similarly the amount of non-sea salt sulfur (nssS) was calculated relative to the sea-salt sodium, ssNa:

162 
$$\mathbf{nssS} = [\mathbf{S}]_{\mathbf{obs}} - [\mathbf{ssNa}] \times \left(\frac{[\mathbf{SO}_4^{-1}]}{[\mathbf{Na}]}\right)_{\mathbf{seawater}}$$
158

130

Where the amount of sulfur relative to Na in sea-water,  $([SO_4^{2-}]/[Na])_{seawater}$  has the constant mass ratio of 0.252 (Millero, 1974). ssNa was calculated by comparison with calcium as both have sea salt and dust origins (Röthlisberger et al., 2002):

164 
$$ssNa = \frac{[Na_{obs} \times R_t - Ca_{obs}]}{[R_t - R_m]}$$
163 (3)

165 Where 
$$R_t$$
 and  $R_m$  are the Ca/Na mean crustal and mean marine mass ratios of 1.78 and 0.038,  
166 respectively, (Millero, 1974).

167 Bromine enrichment factors relative to sea water concentrations were calculated using the following:

$$\mathbf{enrBr}(\mathbf{Na}) = \left(\frac{[\mathbf{Br}]}{[\mathbf{Na}]}\right)_{\mathbf{obs}} / \left(\frac{[\mathbf{Br}]}{[\mathbf{Na}]}\right)_{\mathbf{seawater}}$$

168

169

170 where the ([Br]/[Na])<sub>seawater</sub> mass ratio is 0.00623 (Millero, 1974).

# 171 2.4 Air mass back trajectories

To identify the likely sea ice source regions of MSA and Br deposited at the ice core sites, we perform 10 day air mass back trajectories of boundary layer air masses from each ice core site using the GDAS1 archive dataset in the Hysplit4 software (Draxler and Hess, 1998). The starting height of the back trajectories was 500 m to ensure that the monitored air masses travelled close enough to the surface at the ice core site to potentially deposit aerosols. The vertical velocity field was taken from the

7

(1)

(2)

(4)

177 meteorological data files. Air mass back trajectories were started every 12 hours and allowed to travel 178 for 10 days (total number of trajectories hours = 14400 hours per month). The number of hours that the 179 trajectories spent in a 2°x2° degree grid was summed over all of the trajectories for that month between 180 the years 2005-2013. Previous work showed that the rapid advection of MBL air was the likely source

181 of reactive halogens at Summit (Sjostedt et al., 2007).

# 182 2.5 Sea Ice Correlation mapping

183 In order to assess the relationships between sea ice conditions and ice core chemistry, correlation maps were generated between annual MSA concentrations and monthly sea ice using the HadISST1 ICE 184 dataset at 1° latitude-longitude monthly resolution (Rayner, 2003). Pre-1979 sea ice datasets were 185 interpolated from sea ice extent maps compiled by Walsh (1978) which incorporate a variety of 186 empirical observations. The data were later bias corrected using modern satellite data (Rayner, 2003). 187 188 Correlations were performed separately for the satellite period (1979-2012) and for the extended record (1900-2012), excluding the period 1940-1952 when the record has no variability due to scarcity of data 189 190 (Rayner, 2003). Because strong DMS emissions occur in marginal sea ice zones (Sharma et al., 2012), 191 we considered both sea ice concentration (SIC) and the area of open water in the sea ice pack (OWIP) 192 which represents the size of the marginal sea ice zone. OWIP is defined as the difference between sea 193 ice area (calculated from sea ice concentration over the area of the grid cell) and sea ice extent (NSIDC). 194 A SIC of 15% was used as the threshold for a grid cell to contribute to sea ice extent. The area of OWIP 195 was calculated within the coastal areas as defined by the results of the air mass back trajectories (Sect. 196 3.4).

Outliers were removed from the MSA time series (see Fig. 2) before the correlations were performed. The outliers were removed using the technique described by Sigl (2013) for identifying volcanic signals using a 25 year running average filter. Correlations were performed on an annual rather than seasonal basis because the seasonality of ice core MSA is distorted due to post-depositional migration of MSA signal at depth in the snow pack (Mulvaney et al., 1992) (Fig. 3, S1).

202

#### 203 3 Results

#### 204 **3.1 Bromine**

Ice core measurements of bromine at Summit and Tunu covering the period 1750-2010 are shown in
 Fig. 2. Ice core Br levels at each site were stable until ~1820 at Summit and ~1840 at Tunu when they

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both decreased by ~1 nM, establishing a new baseline that was stable until the mid 1900s. Both ice cores 208 also show a Br peak in the late 20<sup>th</sup> century. The concentration values and the timing of inflections in 209 210 concentrations were determined by a 3 step linear regression of the data set. The analysis was performed by simultaneous linear least squares fitting of 3 straight lines joined by 'inflection points' to the data 211 212 set. The variables of the fitting procedure were the slopes and intercepts of each line as well as the x-213 axis locations at which the total function switched from one linear section to the next (the inflection 214 points). Initial guess values were supplied for each variable to help the fitting procedure reach 215 reasonable values. A summary of the regression results can be found in Table S1.

216 Sea-salt transport onto the Greenland ice sheet occurs predominantly during winter. Historically the 217 winter-time sea-salt maximum was believed to be due to increased cyclonic activity over the open 218 oceans (Fischer and Wagenbach, 1996) though more contemporary studies show that blowing snow 219 from the surface of sea-ice may be a significant source (Rankin et al., 2002; Xu et al., 2013; Yang et al., 220 2008, 2010). At Summit, a winter-time maximum is observed in the most abundant sea salts, Na and Cl 221 (Fig. 3). Bromine also shows a significant winter-time signal, however the annual maximum appears in 222 mid-summer - at concentrations ~70% above winter levels (Fig. 3a). Comparison with Br measured in 223 weekly surface snow samples collected from Summit (from 2007-2013; GEOSummit project) confirms 224 that this summer signal is real and not a result of post-depositional modification of seasonality of the 225 bromine signal (Fig. S2). The results from that study confirm that total Br concentrations peak in 226 summer on the ice sheet closely following the Br cycle observed in the Summit-2010 ice core. In 227 addition to the comparison with the Geosummmit data, in the ice cores studied here there are routinely 228 more than 10 measurements made within a yearly layer of snow giving confidence to the allocation of 229 a summer maximum in bromine at Summit. Analysis of the annual cycle of bromine in the Tunu ice 230 core also shows a summer maximum when averaged over the entire ice core time series but with 231 significantly larger error than observed at Summit. The timing of this peak suggests a predominant 232 summer-time deposition of bromine that dwarfs that from winter sea salt sources.

233 The shape of the annual bromine cycle does change slightly over the course of the Summit record (see 234 Fig. 3). Starting in the early 1900s the annual bromine cycle slowly becomes broader. A slight shift in 235 the maximum from a solely summer peak in the preindustrial era towards a broad summer-spring peak by 1970 is observed (Fig. 3 lower plot). Comparison with the sea salt tracer, sodium, which does not 236 237 undergo the large temporal shift and broadening of its seasonal cycle shows that this change in bromine 238 seasonality is not linked to changes in production or transport of sea-salt aerosols or even dating 239 uncertainties in the ice core but perhaps the introduction of an additional, smaller bromine source in the 240 spring-time during the industrial era.

241 Both ice cores show a predominantly positive Br enrichment throughout the year (Fig. S3, S4) relative 242 to both sea salt elements chlorine and sodium. This enrichment reaches a maximum in mid to late 243 summer at Summit (Fig. 3). We assume that this enrichment reflects Br enrichment in the aerosol transporting Br to the ice sheet. In a comprehensive review of global aerosol Br measurements, Sander 244 245 et al. (2003) concluded that in general, aerosols which showed positive Br enrichment factors were of 246 sub-micrometer size. These small aerosols can travel further (lifetimes of around 5-10 days) and due to 247 their larger surface/volume ratio may experience more atmospheric processing than larger aerosols, 248 resulting in the positive enrichment. However, post-depositional reduction of the bromine concentration 249 is a possibility during the summer months due to photolytic processes at the snow surface. This may be 250 the cause of the noisiness of the bromine signal within the lower accumulation, Tunu core. However, 251 the increased snow accumulation that occurs during the summer months in both central and northern 252 Greenland (Chen et al., 1997) should act minimise these bromine depleting effects driven by increased 253 insolation in summer and indeed Weller (2004) has shown that accumulation rates of this size are large 254 enough to prevent the post-deposition loss of other species such as nitrate and MSA.

255 Both sites also show a (small) positive enrichment of chlorine relative to sodium, which is amplified at 256 small sodium concentrations. Chlorine containing aerosols are expected to undergo similar chemical 257 processing to bromine containing aerosols but the enrichment factors of bromine (relative to sodium) 258 are much larger which is likely due to the high solubility of bromine species such as HBr (Sander et al., 259 2003). Alternatively, the chlorine enrichment could be interpreted as a sodium depletion of the aerosols 260 particularly in those of small diameter where both concentrations are low; this would amplify the 261 bromine enrichment (relative to sodium) but would not explain the bromine enrichment relative to 262 chlorine. It is likely that both halogens undergo some degree of enrichment and the sodium undergoes 263 some depletion in the aerosols though it is difficult to determine this from the data.

A summer-time maximum in Br enrichment was also observed by Spolaor (2014) in a short segments of Antarctic Law Dome ice core as well as two Arctic ice cores. Spolaor et al. believe that the main source of the inorganic bromine originated from spring-time bromine explosion events above sea ice and the summer-time maximum could possibly be an indication of lag-time between bromine containing particles becoming airborne and their deposition. Further investigation is needed to definitively establish the seasonality of bromine deposition at the poles. However the results of the Arctic ice cores studied here suggest that the summer maximum in bromine deposition is indeed real.

In the Tunu ice core, 11% of the monthly bromine enrichment measurements relative to Na were negative (less than the Br/Na seawater ratio, Fig. S3) and 12% were negative relative to Cl. It is possible

- that the negative enrichment values observed in the Tunu ice core are therefore a result of larger aerosols
- 274 (> micrometer) reaching the site due to its proximity to the coast (and thus the likely sea ice aerosol
- 275 source region) in comparison to Summit.

### 276 3.2 MSA

The Summit-2010 MSA record (Fig. 2) replicates that measured by Legrand in 1993 (Legrand et al., 277 278 1997) and extends it an additional 17 years (see Fig. S5). The mean Summit-2010 MSA measurements 279 over the period 1984-1992 (2.0 $\pm$ 0.7 (1 $\sigma$ ) ppb) also compare well with the results of the sub-annually 280 sampled Summit snow pit study performed by Jaffrezo et al., (1994); 2.1±1.8(10) ppb. Both the Legrand 281 and Jaffrezo studies measured MSA using ion chromatography of discretely sampled snow and ice. The similarity between the Summit-2010 measurements and the results of these studies demonstrates that 282 the new, continuous technique is able to achieve a comparable accuracy in MSA measured 283 284 concentrations to the traditional, discrete technique. It also demonstrates that negligible amounts of 285 MSA are being lost by using the continuous melt method.

The Tunu measurements represent the first MSA profile at this location. Replicate measurements of the entire Tunu ice core were performed with the on-line, continuous technique by melting a secondary stick of ice cut from the original Tunu ice core. The replicate measurements closely followed the original MSA measurements demonstrating the reproducibility, stability and high precision of the continuous MSA technique (Fig. S6). The Tunu MSA record was also reproduced using discrete samples collected from the CFA system (Fig. S7).

At Summit, MSA concentrations averaged 48 nM in the late 18th century, compared with just 27 nM at 292 293 Tunu. From 1878-1930 MSA concentrations at Summit plateaued at 36 nM after which they began to 294 drop rapidly, at a rate of 0.27 nM/year, reaching 18 nM by 2000 C.E., Large fluctuations in the MSA 295 record after this time make it difficult to assess the most recent trend in Summit MSA concentrations. 296 MSA concentrations in the Tunu core showed a similar temporal variability to those in the Summit 297 record, and until the mid-20<sup>th</sup> century, were consistently lower in magnitude. MSA concentrations only began to decline consistently at Tunu after 1984, almost 50 years after the rapid decline observed in the 298 299 Summit record. After 2000 C.E., large fluctuations in concentration were again observed making the 300 modern-day trend in MSA concentration at Tunu difficult to establish.

301 Comparison with the total sulfur record (Fig. 4) reveals that during the preindustrial period, MSA 302 contributes to  $\sim$ 12% and  $\sim$  7% of the total sulfur signal at Summit and Tunu, respectively, compared 303 with < 2% at the height of industrial period (1970 C.E.) at both sites.

The low frequency, preindustrial trend in MSA concentrations seen in these ice core records closely follows that of bromine; particularly distinct is the decrease in both MSA and bromine at both sites in the early to mid 1800s (Tables S1 and S2). In the 1900s, however, both sites show a divergence between the MSA and Br records—as MSA begins to decline, Br concentrations increase.

308 A dramatic shift in the 'timing' of the annual MSA maximum in Summit-2010 ice core is illustrated in 309 Figs. 3c and S1. The signal shifts gradually and continuously along the length of the the entire Summit-310 2010 record from a spring to winter maximum (Fig. S1). This phenomenon has previously been 311 observed in several Antarctic ice cores and has been attributed to post-depositional migration within the 312 ice due to salt gradients (Mulvaney et al., 1992; Weller, 2004). At very low accumulation ice core sites 313 post-depositional loss of MSA (and nitrate) must also be considered. Extrapolation of data collected by 314 Weller (2004) from a series of East Antarctic ice cores predicts that sites with annual average accumulations of greater than 105 kg m<sup>-1</sup> yr<sup>-1</sup> (0.105 m yr<sup>-1</sup>) will not show post-depositional loss of 315 316 MSA (or nitrate). Both ice cores in this study have sufficient average annual accumulation that post-317 depositional loss of MSA (and nitrate) is predicted to be negligible and so is not discussed further.

# 318 3.3 Acidic Species

319 In winter, with the collapse of the polar vortex, polluted air masses enter the Arctic region as the 320 phenomenon known as the Arctic haze (Barrie et al., 1981; Li and Barrie, 1993).  $SO_2$  and  $NO_x$  from the 321 haze are adsorbed onto aerosols or deposited directly on the ice/snow and oxidised to sulfuric  $(H_2SO_4)$ 322 and nitric acid (HNO<sub>3</sub>). There are also natural sources of SO<sub>2</sub> (biomass burning, volcanic eruptions, oceans (Li and Barrie, 1993; McConnell et al., 2007; Sigl et al., 2013) and NO<sub>x</sub> (microbial activity in 323 soils, biomass burning, lightning discharges (Vestreng et al., 2009) as well as other snow/ice acidifiers 324 325 including MSA, hydrogen chloride and organic acids released from biogenic or biomass burning sources 326 (Pasteris et al., 2012).

The annual cycle for nitrate  $(NO_3^-)$  is shown in Fig. 3d. Before 1900 C.E. the nitrate shows a seasonal 327 328 maximum in late summer/early fall after which the maximum shifts to late spring/early summer. 329 Although there are biological sources of nitrate in the ice core aerosol source regions, in a recent study focused on the  $NO_3^-$  and  $\delta^{15}N - NO_3^-$  record in the Summit-2010 ice core, Chellman et al. (2016) 330 331 concluded that the preindustrial (1790-1812 C.E.)  $NO_3^-$  seasonal cycle was driven by biomass burning 332 emissions. However, in the modern era (1930-2002 C.E.) oil-burning emissions became the dominant 333 source of  $NO_3^-$  in the snow-pack. The change in the dominant  $NO_3^-$  source due to industrialisation is the 334 cause of the shift in timing of the seasonal cycle.

Total snow acidity was stable at both sites from 1750 through to ~1900 C.E. except for sporadic, short-335 lived spikes due to volcanic eruptions. The average preindustrial acidity was the same at both sites (~1.8 336 μM). Both records also show two distinct maxima in acidity centred on 1920 and 1970 C.E. (Fig. 4) 337 with Tunu displaying higher acidity than Summit over the entire industrial period. Overlaid with the 338 339 acidity is the total sulfur (S) record for both ice cores. The high correlation between the acidity and S records illustrates that the sulfur species are the dominant natural and anthropogenic acidic species in 340 the ice cores. The trend in acidity closely follows the global  $SO_2$  emissions with maxima from coal 341 (~1920 C.E.) and coal plus petroleum combustion (~1970 C.E.), respectively (Smith et al., 2011). After 342 343 1970 the records of acidity and S deviate. This deviation can be attributed to the presence of nitric acid that remains at a relatively high concentration in the late 20<sup>th</sup> century whilst sulfur species reduce in 344 345 concentration (Fig. 4).

346  $NO_3^-$  concentrations show no trend during the preindustrial era in either ice core records, averaging 347 1.1(±0.02) μM and 1.3(±0.03) μM for Summit and Tunu, respectively. The higher signal-to-noise ratio 348 in the Summit-2010 record reveals a small peak in  $NO_3^-$  concentrations centred on ~1910. The Tunu record also shows elevated  $NO_3^-$  concentrations over this period. However the large variability in the 349 signal makes it difficult to establish a higher resolution temporal trend. Both records clearly show a 350 351 large increase in  $NO_3^-$  after 1950, peaking in ~1990 and followed by a general decreasing trend with the 352 average  $NO_3^-$  levels still double that of preindustrial concentrations: 2.1µM and 2.3 µM at Summit and 353 Tunu, respectively.

The nitrate records from both sites follow the trend in northern hemisphere  $NO_x$  emissions with a peak in ~1910 and 1990 C.E.– a result of emissions from increases in both Northern Hemisphere fertilizer

usage and biomass and fossil fuel combustion (Felix and Elliott, 2013).

#### 357 3.4 Air mass back trajectories

Air mass back trajectory results demonstrate that air masses reaching the Summit-2010 site between March and July originate primarily from the South/South-East of the ice core site (Fig. 5a). Previous back trajectory analyses by Kahl *et al.* (1997) also linked individual spikes in their Summit MSA record to air masses that had passed over this same region of coast (SE Greenland) within the previous 1-3 days. Similar back trajectories were calculated for Summit-2010 up to heights of 500 and 10,000m (total column trajectory, Fig. 5a, S8a) illustrating that air masses that travel in the free troposphere and lower troposphere follow similar back trajectories and likely share the same source regions.

The results for Tunu indicate that air masses arrive primarily from the west coast of Greenland, passing over the Baffin Bay area, but there is also significant contribution from both the SE and NE (in May) coastal areas (Fig. 5b, S8b). Of these two secondary areas it is likely that aerosols transported from the NE would have a greater influence on the ice core concentrations due to proximity to the ice core site. Aerosol deposited at Tunu therefore represents a mixture of source regions, but are likely dominated by the NW Greenland, Baffin Bay coastal region.

#### 371 3.5 MSA - Sea Ice correlations

Locations which showed a sea ice concentration (SIC) variability greater than 10% (the average 372 estimated range of uncertainty in the satellite measurements) and have a significant correlation to MSA 373 374 (t-test, p<0.05) are displayed in Figs S9 and S10 for the months of March-July. A greater weight must be placed on the post-1979 sea ice concentration maps as these were derived from passive microwave 375 376 satellite data and, where available, operational ice chart data. The likely air mass source regions, as 377 defined by the results of the air mass back trajectories, are indicated by the black bordered regions. 378 Within these areas there is generally a negative correlation between SIC and MSA, particularly in the 379 spring months and only small patches that show large correlation ( >0.4). The large areas of positive correlation along the east coast and in the western Barents Sea are striking for the Summit-2010 record, 380 381 however, these areas are outside of the defined air mass source region and thus are unlikely to be 382 contributing to the ice core aerosol records. The positive correlation is likely an artefact of the negative autocorrelation between sea ice conditions in this region and the SE coast source region (Fig. S11). 383

The effect of the estimated error in dating of the MSA records on the SIC correlation maps is explored in Fig. S12. By shifting the dating of the MSA records to either extreme of the dating error estimate and replotting the SIC correlation plots it is clear the error in the dating of the MSA records does not affect the sign of the correlations displayed on the maps but can have an affect on the magnitude of the correlation found in different locations. This is likely a result of the peaks in the MSA record being shifted in or out of temporal coherence with peaks in SIC at the different locations.

Over the period 1900-2010 C.E. highly significant correlation (t-test, p<0.001) is found between the annual ice core MSA and the amount of open water in the ice pack (OWIP, representing the area of the marginal sea ice zone, Figs. 6a and 7a; lower plots) in these aerosol source areas. For both ice cores the source region OWIP trend is followed by the MSA. In the Summit-2010 ice core the highest correlation between annual MSA and monthly OWIP occurs in May (r=0.58, p<0.001) though the following months through to July all show highly significant correlations (July r=0.53, p<0.001). For comparison, the May

SIC correlation map is also shown as the upper plots in Figs. 6a. Figs. 3f and S13 demonstrate that this time period (May-July) corresponds to the peak and then rapid decline in the amount of annual OWIP within the Summit-2010 aerosol source area because of the decreasing extent of sea ice. Rapid loss of sea ice reveals areas of biological activity previously capped by the ice allowing surface-atmosphere exchange of DMS, resulting in the seasonal peak in atmospheric MSA correlation with the peak in the area of OWIP.

402 At Tunu the highest correlation over the 1900-2012 C.E. period is found between annual MSA and 403 annual OWIP (r=0.59, p<0.001), though the July OWIP shows the highest monthly correlation and is also highly significant (r=0.41, P<0.002). For comparison, the July SIC correlation map is also shown 104 405 as the upper plots in Figs. 7a. Due to the more northerly location of the Tunu aerosol source region, the 406 sea ice pack in this region is generally less fractured and break-up occurs later in the year, with a sharp peak in OWIP occurring in July (Fig. S13). The higher stability of the ice pack throughout the year 407 408 compared to that in the Summit-2010 source region is the likely reason the Tunu MSA shows highest 409 correlation with the annual average of the OWIP. However, like Summit-2010 the highest monthly 410 OWIP correlation occurs between the annual MSA and the timing of the maximum in annual OWIP 411 (July).

412 Over the shorter, satellite era (1979-2012 C.E.) again Tunu shows strongest correlation between annual 413 MSA and annual OWIP though at a much lower significance (r=0.32, p<0.05), and the highest monthly 414 correlation occurs in March (r =0.2, p<0.1) albeit with low significance. The significance of the Tunu 415 correlation over this period can be dramatically increased (annual OWIP r=0.54; p<0.001, March OWIP 416 r=0.63, p<0.001) if the closer, secondary aerosol source region (NE Greenland, 80°-73°N, 20°-0°W) 417 is assumed to also influence the site in equal proportion. March corresponds to the timing of increased 418 insolation and thus the rapid increase in ice algal production (Leu et al., 2015). The shift from a July to 419 March peak in the correlation of OWIP with annual Tunu MSA may be a result of the reduced overall 420 SIE (and thus OWIP) influencing the timing of MSA production. Unfortunately, the post-depositional 421 migration of the MSA signal within the ice cores masks any evidence of true seasonal MSA shifts. 122 Summit-2010 also shows a much less significant monthly OWIP correlation with the annual MSA signal 423 over this time period, with the most significant correlation again occurring in March (r = 0.4, p < 0.02). The greater significance of both the SIC-MSA and OWIP-MSA correlations at both sites over the longer 124 425 time period is likely a result of the averaging of any MSA production or transport variability as well as the dominance of the low frequency variability of both time series on the overall correlation. 426

#### 427 3.6 MSA and bromine relationship

128 In an era where climate is driven by only natural forcings, chemical species that share a common source

- should show broadly consistent variability. This is evident in the preindustrial section of both ice core
- 430 records where the relationship between MSA and Br (monitored as Br/MSA) remains constant over the
- 431 entire period (Fig. 4) despite individual records going through step function changes. Using a 25 year
- running average on all records, the correlation between MSA and Br over the preindustrial period was
- 433 calculated as: Summit-2010: r=0.282 (p=0.0008); Tunu: r=0.298 (p = 0.0004), n= 138. After ~1930 434 C.E., relative increases in Br concentrations cause the Br/MSA ratio to increase above the stable
- t35 preindustrial levels by more than 160%, reaching a peak in ~2000 C.E. at both sites.
- Bromine in excess of what is expected from a purely sea ice source (non sea ice bromine, nsiBr) was 436 437 calculated by comparison to the other sea ice proxy, MSA. A linear regression of MSA versus Br was 438 performed with the preindustrial data (1750-1880 C.E.) to establish the relationship between the two proxies during an era free of anthropogenic forcing (Figure S14a,b). This relationship was then 439 140 extrapolated into the period after 1880 C.E. in order to estimate the amount of bromine sourced only 441 from sea ice sources during the industrial era. The MSA record was smoothed with a 9<sup>th</sup> order 142 polynomial function before being used in the extrapolation to reduce the noise in the resultant record 443 whilst maintaining the low frequency trends (Figure S14c,d). nsiBr is thus the difference between the 144 total bromine measured and the calculated, natural sea ice bromine (Figs. 8 and S14e,f); in contrast to Brexc defined by Spolaor (2016) as the amount of bromine in excess of the Br/Na seawater ratio. 145
- An estimate of the nsiBr is shown in Figs. 6,7 and 8. By definition, nsiBr is essentially constant during
  the preindustrial period, but during the industrial period nsiBr peaks, reaching a broad maximum
  between 1980-2000 C.E. of ~3.4nM and 1.9nM at Summit and Tunu, respectively.

#### 449 **4** Discussion

450 The significant correlation between variability of marginal sea ice zone (OWIP) area within the 451 identified source regions and the MSA records suggests that MSA records can be used as a proxy for 452 modern sea ice conditions in these areas. North Atlantic Oscillation (NAO) proxy records developed in Greenland ice core records (Appenzeller et al., 1998) suggest that although the northern hemisphere 453 154 climate phenomenon has shown variability over the past 200 years, its effect is damped in Northern 455 Greenland (Appenzeller et al., 1998; Weißbach et al., 2015) so we can assume that no major changes in 456 atmospheric circulation patterns have occurred to change the source regions for the marine aerosols between the preindustrial and industrial periods. If this assumption is true, our identification of MSA as 457 a sea ice proxy (specifically a marginal sea ice zone proxy) may be valid for time periods both before 458

and after 1850 at each ice core site.

460 The MSA records reveal that after 1820 C.E. a gradual decline in sea ice occurred along the southern 461 Greenland coast (reflected in the Summit-2010 core) and that this decline in sea ice did not extend 462 significantly to the most northern Greenland coastline (reflected in the minimal change in Tunu MSA 463 during this period). It is not unexpected that the Summit-2010 record would show the most dramatic 164 changes in sea ice since we have demonstrated that the Summit sea ice proxy (MSA) is sourced from 465 the south-east Greenland coast - an area sensitive to climate changes as it is primarily covered by young, fragile sea ice. The timing of the sea ice decline is coincident with the end of the Little Ice Age, identified 466 from  $\delta^{18}$ O ice core records as spanning the period 1420-1850 C.E. in Greenland (Weißbach et al., 2015). 467 The dramatic dip in sea ice reflected in both the Tunu MSA and Br records at 1830 C.E. (and also seen 468 less dramatically in Summit) also appears in the multi-proxy reconstruction of sea ice extent in the 469 470 Western Nordic Seas performed by Macias Fauria et. al. (2010). This may be evidence of a 1830 C.E. sea ice decline event isolated to the east Greenland coast as the ice core records do not replicate the 471 other dramatic, early 20th century fluctuations observed in the latter part of the Western Nordic Seas 472 473 reconstruction.

174 From the ice core records it appears that the greatest decline in Greenland sea ice began in the mid 20th 475 century, dropping to levels that are unprecedented in the last 200 years. This decline is observed along 176 the entirety of the Greenland coast. Sea ice declined first around the southern coast (from 1930 C.E., 177 reflected in Summit-2010) followed 54 years later by the more northern coastline (reflected in the Tunu 478 record, see infection timings in Table S1). This sea ice decline is coincident with the sustained increase 479 in greenhouse gases which has been identified as the major climate forcing and driver of increased global temperatures during the 20th century (Mann et al., 1998) and follows the same general trend in 480 Arctic wide sea ice extent observed by Kinnard (2008). 481

482 Bromine (more specifically bromine enrichment (Spolaor et al., 2014) and bromine excess (Spolaor et 483 al., 2016)) has also been suggested as a possible proxy for sea ice conditions, however the timing of the 184 largest bromine aerosol deposition, in summer, does not coincide with the largest growth or extent of 485 new sea ice. Sea ice begins to increase only at the end of summer as the fractures in the ice cover are re-laminated and the ice edge begins to advance southward (see Fig. 3f). Fig. S4 compares the record 486 487 of total bromine and bromine enrichment (calculated relative to sodium, enrBr(Na)) from the Summit-488 2010 ice core. The major discrepancies between the two records occur when the total sodium signal has 489 sharp maxima causing dips in the enrBr(Na) record in ~1954 and 1990 C.E. and the magnitude of the 490 low frequency variability in enrBr(Na) is not as great as in the total bromine record. This is also

491 demonstrated in figs. 6 and 7 where the enrBr(Na) records are compared with the OWIP records. Whilst 492 both series share high frequency temporal features, over the longer term (1900-2010) the low frequency 493 trend is dramatically different. We are not discounting enrBr(Na) as a viable proxy for sea ice 494 conditions, however the use of Na to try and extract the pure sea water component of the Br is 495 complicated by the fact that a lot of Na comes from the sea ice surface as well as from the open ocean. 496 Na itself has been used as a sea ice proxy in several prominent studies (Wais Divide Project Memebers, 497 2013; Wolff et al., 2003) because, like Br, Na is incorporated into the snow on the surface of the sea ice 498 and can be subsequently blown aloft to produce the atmospheric Na signal seen in the ice core. In 199 addition, the Na concentration is fractioned upon the formation of the ice when mirabilite (Na<sub>2</sub>SO<sub>4</sub>) is 500 precipitated out of the brine solution at -8°C (Abbatt et al., 2012).

501 The calculated, non-sea ice bromine records (nsiBr) for both ice cores are shown in figs. 6 and 7. Like 502 the enrBr(Na) records, the nsiBr records share some of the high frequency features of the OWIP records, 503 however there is no significant correlation between nsiBr and the selected OWIP records over the short 504 time period. This supports the supposition that the nsiBr record is indeed an extraction of the non-sea 505 ice component of bromine from the total bromine record. Over the longer time period there is a 506 significant negative correlation between OWIP and nsiBr at both sites (Summit-2010: r=-0.7, p<0.001, 507 Tunu: r=-0.22, p<0.02). This result is likely an artifact of the positive correlation from the MSA records 508 used to generate the nsiBr records.

509 So what is the summer-time source of bromine? What is the cause of the increase in spring-time bromine 510 explosion events in the industrial era? (see Fig. 3, lower panel) and why does the bromine record deviate 511 from the sea ice proxy record (MSA) around the same time? Possible sources of bromine and the factors 512 which may effect the resultant bromine deposition flux are discussed below.

#### 513 4.1 Alternate sources of bromine

#### 514 4.1.1 Combustion of coal

Bromine is present in coal (Bowen, 1979; Sturges and Harrison, 1986) and coal burning is therefore a potential source of increased bromine deposition on the Greenland ice sheet over the period 1860-1940 (McConnell and Edwards, 2008). McConnell et al. (2007) demonstrated that pollution from the Northern American coal burning era was deposited all over Greenland leaving as its fingerprint large amounts of black carbon and toxic heavy metals. Sturges (1986) measured the relative concentrations of Br and Pb in particulates emitted from the stacks of coal fired power stations and found a molar ratio (Br:Pb) ranging between 0.36-0.67:1. Figure 8 illustrates that at both Summit and Tunu the exPb (lead 522 not from dust sources) preserved in the ice cores over the coal burning era ( $\sim$ 1920) was less than 1nM.

523 This concentration implies that the upper limit to the amount of bromine deposited from coal

524 combustion would be 0.67nM (assuming no loss of bromine from the particulates during transportation).

525 This is an insignificant amount compared to the total Br signal preserved in the ice at this time. Coal

526 combustion is not the major cause of the elevated industrial Br concentration.

# 527 4.1.2 Leaded Gasoline

528 The largest global, historical, anthropogenic source of bromine is thought to be the combustion of leaded 529 gasoline. Large quantities of 1,2-dibromoethane (DBE) were added to leaded fuel as a scavenger for Pb 530 preventing lead oxide deposition by converting it to volatile lead bromide salts as well as  $CH_3Br$  (Berg 531 et al., 1983; Nriagu, 1990; Oudijk, 2010). In 1925 C.E. gasoline had a Br:Pb molar ratio of 2:1 in a formulation which is now called "aviation fluid". The Br:Pb molar ratio was reduced to 1:1 in the 1940s 532 533 except in places such as the Soviet Union which continued to use "aviation fluid" for motor gasoline 534 (Thomas et al., 1997). Although the consumption of leaded gasoline has been well documented, 535 particularly in North America, the estimates of the emissions of bromine compounds from the 536 combustion process are still unclear. Estimates of the amount of DBE that is converted into gaseous CH3Br range from 0.1% to 25% (Bertram and Kolowich, 2000) and direct measurements of exhaust 537 fumes across NW England found a Br:Pb ratio of between (0.65-0.8):1 in the airborne particulates 538 539 (Sturges and Harrison, 1986).

The ratio of Br:Pb in the gasoline formulae can therefore be used only as an upper limit to predict the 540 541 Br:Pb ratio in gasoline combustion aerosols transported to the ice core sites. Figure 8 shows a comparison between nsiBr and exPb measured in each ice core. Also illustrated is the upper limit of the 542 543 amount of bromine expected from gasoline sources assuming the 2:1 Br:Pb ratio for aviation gasoline 544 over the whole leaded gasoline era. World-wide leaded gasoline emissions were estimated to have 545 peaked in 1970 C.E. (Thomas et al., 1997)-an assumption that is supported by the observed timing of the exPb maximum observed in both ice cores. Whilst it is likely that leaded fuel contributed to the 546 547 increased bromine observed between 1925 and 1970, it is clear that it was not the only contributor to 548 the nsiBr record, particularly after 1970 when the nsiBr record continues to rise despite a worldwide 549 decline in leaded fuel consumption. The disparity between the exPb and nsiBr records suggests the driving force for the enhanced emission of Br was still active and increasing after 1970. 550

#### 551 4.1.3 Seasonal salinity changes

552 Younger sea ice surfaces such as frost flowers, new and 1<sup>st</sup> year sea ice have a higher salinity and thus

- 553 have higher bromine concentrations than older sea ice surfaces (Hunke et al., 2011). The salinity of sea
- ice is at its maximum at the start of the winter season after which surface salinity slowly diminishes due to gravitational draining (Hunke et al., 2011). As summer approaches, ice continues to undergo desalination due to melting of surface snow which percolates through the ice (Hunke et al., 2011).
- 557 Satellite observations that the BrO flux from the sea ice declines over summer (despite increasing 558 insolation) is likely due to the combined reduction in young sea ice area and in ice salinity. Ocean 559 surface salinity decreases in the summer due to the increased meteoric water flux and melting of 560 desalinated sea ice. Salinity increases are therefore unlikely to be the sole cause of the nsiBr flux
- 561 observed in the ice core records and the observed summer maximum in bromine.

### 562 4.1.4 Organic bromine species

Gaseous bromocarbons can be a source of inorganic bromine to the snow pack when they react with •OH or to a lesser extent with  $\cdot NO_x$  or by photolysis (Kerkweg et al., 2008; WMO, 1995) to form the less reactive species *HBr*, *BrNO*<sub>3</sub> and *HOBr*. These species can then be washed out of the atmosphere and deposited on the snow surface due to their high solubility (Fan and Jacob, 1992; Sander et al., 1999; Yung et al., 1980).

- 568 The predominant source of gaseous bromine in the atmosphere is methyl bromide,  $CH_3Br$  (WMO, 569 2002). The major modern sources of  $CH_3Br$  are fumigation, biomass burning, leaded fuel combustion, 570 coastal marshes, wetlands, rapeseed and the oceans (WMO, 2002). The ocean is also a major sink for 571  $CH_3Br$ , the temperature sensitive dissolution occurring through hydrolysis and chloride ion substitution to form bromide (WMO, 1995). ~30% of  $CH_3Br$  was from industrial emissions at the time of the global 572 peak in the  $CH_3Br$  mixing ratio (1996-1998) (Montzka and Reimann, 2010). The timing of the massive 573 574 increases in nsiBr seen at both ice cores sites coincides with the timing of maximum anthropogenic emissions of  $CH_3Br$ . However, the estimated 2.7 ppt increase in global tropospheric  $CH_3Br$  above 575 576 preindustrial levels equates to only  $\sim 3.7$  ppt (0.05nM) Br incorporated into the snow pack (assuming 577 100% conversion efficiency of  $CH_3Br$  in soluble Br species). This level is far less than the 2-5 nM 578 increase in nsiBr observed in the ice cores during the industrial period.
- 579 Bromoform (*CHBr*<sub>3</sub>) is emitted from vegetation such as marine phytoplankton and seaweed. It has the 580 largest globe flux of all the bromocarbons (estimated at almost 5 times that of  $CH_3Br$  (Kerkweg et al., 581 2008). However, it is very short-lived (atmospheric lifetime of ~ 17 days (Ordóñez et al., 2012) and 582 thus is confined to the marine boundary layer. Inorganic bromine formed from the destruction of *CHBr*<sub>3</sub> 583 would therefore be representative of only local sources of organic bromine. The biological seasonal 584 cycle maximises the production of *CHBr*<sub>3</sub> in summer and concentrations are greatly reduced but not 20

585 negligible in winter (tidal forcing also influences bromocarbon emission by allowing coastal algae to dry-out (Kerkweg et al., 2008). The season of Arctic sea ice algae productivity is confined by limitations 586 587 in available sunlight and nutrients resulting in a mid-to-late spring maxima - depending upon site location (Leu et al., 2015) - as is reflected in the seasonality of the MSA record. Direct transport of 588 589 bromine enriched aerosols from these algal sources to the ice core sites again cannot explain the summer 590 maximum of bromine observed in the ice. In addition to the incoherence of the seasonality of the 591 bromine ice core signal, to-date biogenic sources have been considered insignificant sources of bromine 592 in the Arctic marine boundary layer compared with the inorganic bromine source from sea salts 593 (Simpson et al., 2007).

#### 594 **4.2** Cause of the spring-time increase in bromine flux

# 595 4.2.1 Bromine explosion events

596 Spring is the time of 'bromine explosion' events above sea ice. Sea salt aerosols passing through these 597 BrO plumes can become enriched with bromine by adsorbing the gaseous species (Fan and Jacob, 1992; Langendörfer et al., 1999; Lehrer et al., 1997; Moldanová and Ljungström, 2001; Sander et al., 2003). 598 Nghiem (2012) showed that these bromine rich air masses can then be elevated above the planetary 599 500 boundary layer and transported hundreds of kilometres inland. Increasing the frequency and duration of 501 the bromine explosion events would therefore likely increase the amount of bromine delivered to the 502 ice core sites during spring without influencing the total aerosol flux and thus explain the shift in the 503 bromine seasonal concentrations from a purely summer to a broad spring-summer maxima (Fig. 3).

504 Spring-time field studies at Ny Ålesund, Svalbard have shown positive correlation between atmospheric 505 filterable bromine species and elevated levels of sulfate and nitrate (Langendörfer et al., 1999; Lehrer 506 et al., 1997) suggesting that acidic, anthropogenic pollution may be the driver of the observed increases 507 in annual bromine enrichment during the industrial period and seasonal shift.

# 508 4.2.2 Acidity effects on debromination

In remote, relatively clean environments such as the Arctic, even small increases in acidity are thought to affect the cycling of bromine in the snow pack (Finlayson-Pitts, 2003; Pratt et al., 2013; Sander et al., 1999). In the laboratory, increasing the acidity of frozen (Abbatt et al., 2010) and liquid salt solutions (Frinak and Abbatt, 2006; George and Anastasio, 2007) increased the yield of gas-phase  $Br_2$  whilst at the same time increasing the *solubility* of other bromine species, such as *HBr*. The uptake efficiency of

514 HBr by acidic sulfate aerosols, for example, is estimated at 80% compared to 30% for sea salt aerosols 515 (Parrella et al., 2012). Interestingly, Abbatt (1995) demonstrated that HBr is more than 100 times more soluble in super-cooled sulfuric acid solutions than HCl. This may explain the cause of bromine 516 enrichment in the aerosol measured in the ice cores relative to the more abundant chlorine (Fig. S3). 517 518 The results of both the laboratory and field studies suggest that increasing snow/ice acidity in the Arctic 519 will likely enhance spring-time bromine explosion events above the sea ice whilst the increase in 520 solubility allows the termination products of the explosion to be transported away from the sites on the 521 surface of acidic aerosols. Increasing spring-time bromine aerosol concentrations would increase the 522 average annual bromine concentrations deposited on the ice sheet and could explain the nsiBr records 523 observed in both ice cores.

There are also significant periods over which the calculated nsiBr record shows negative values (e.g. 524 525 1815-1870 C.E. in Summit-2010 and 1860-1940 C.E. in Tunu). The negative values are a result of the Total Br being less than that calculated by interpolation from the smoothed MSA record. Though the 526 527 sources of Br and MSA are linked - which is what provides the similarities between the general low 528 frequency trend of the two species, the atmospheric processing, transport and deposition of the two 529 species may be modified by different variables such as changes in atmospheric acidity, for example. 530 These variables cause the short term differences between the MSA and Total Br records preserved in 531 the ice so we believe it is not unreasonable to expect negative values in the calculated non-sea ice Br 582 record when the MSA and Total Br are close (essentially no nsiBr).

Figure 9 illustrates that of the two dominant acidic species preserved in the ice,  $HNO_3$  (represented by 533 nitrate) shows the highest correlation to total bromine over sub-decadal time scales at both ice core sites. 534 535 Records were detrended with an 11 year running average before comparison to isolate the high frequency components of each record. The bromine - sulfuric acid (represented by sulfate) correlation 536 537 is not significant. This is primarily because there is no bromine response to the dominant volcanic sulfate spikes throughout the record. The large spikes in sulfate concentrations did not cause a depletion of 538 539 bromine preserved in the snowpack (Figure 9). This result might be expected if the increased acidity 540 caused more bromine to volatize. These results suggest that HNO<sub>3</sub> is the most influential of the MBL acidic species in the processing and transport of Br on aerosols in the MBL. 541

### 542 4.2.3 NOx and links to bromine

543 The snow and atmospheric chemistries of bromine and nitrate  $(NO_3^-)$  are tightly linked.  $NO_3^-$  is one of

the main sources of the •OH radical. The •OH radical can oxidize bromide salts and cause the release

of gas-phase bromine species (Abbatt et al., 2010; Chu and Anastasio, 2005; George and Anastasio,

22

**Deleted:** The periods of negative nsiBr do correspond to the timing of increased sulfate concentrations (due to volcanic or industrial activity) and this could be an indication that the atmospheric sulfate concentrations do have some influence on the production of either the MSA or Br records.

551 2007; Jacobi et al., 2014). Morin et al. (2008) observed that the majority of nitrate that is deposited to the snow surface is of the form  $BrNO_3$  in coastal Arctic boundary layer.  $BrNO_3$  forms by gas-phase 552 553 reaction of BrO and NO<sub>2</sub>. BrNO<sub>3</sub> is quickly adsorbed back onto the snow and aerosol surfaces due to 554 its high solubility. The heterogeneous hydrolysis of  $BrNO_3$  to again release bromine species back into 555 the gas-phase has also been observed (Parrella et al., 2012) and can occur both during sunlight hours as 556 well as in the dark (Sander et al., 1999). However, the study of Thomas et al. (2012) into the cycling of  $NO_{\rm r}$  and bromine species in the snowpack at Summit concluded that the presence of snow  $NO_{\rm s}^{-1}$  would 557 suppress the emission of BrO from the snow pack and into the interstitial air. 558

559 In spring, when the greatest concentrations of BrO are observed over the sea ice the atmospheric concentrations of  $NO_x$  species is rising. After 1900 C.E. there was, on average, a 60% increase in spring 560  $NO_3^-$  concentrations observed in Summit-2010 ice core (Fig. 3d) which, as discussed in Sect. 4.2.1, if 561 reflected in the concentration of acidic aerosols landing on the sea ice (specifically HNO3 562 563 concentrations) would enhance the emission of BrO into the MBL. Satellite imagery shows that bromine in the form of BrO is confined primarily to the atmosphere above sea ice (Schönhardt et al., 2012; 564 Wagner et al., 2001) but the presence of measurable bromine concentration hundreds of kilometres 565 inland preserved in the ice cores demonstrates that the bromine must be transported inland, just not in 566 567 the form of BrO. The reaction of atmospheric  $NO_2$  with BrO can produce the highly soluble  $BrNO_3$ which will preserve the bromine in the aerosol allowing it to be transported inland. If there are high 568  $NO_3^-$  concentrations at the deposition site this will aid in fixing the bromine into the snow pack. This is 569 supported by the observation that  $NO_3^-$  snow pack concentrations reach a maximum in summer, 570 coherent with bromine snow pack concentrations even though maximum Br emission from the sea ice 571 572 occurs in spring. So it appears that  $NO_x$  in its different forms, as  $NO_2$ ,  $NO_3^-$ ,  $HNO_3$ , or  $BrNO_3$  is 573 intertwined with Br as it cycles between the gas and condensed phases and as it is transported from sea 574 ice source to deposition site. Elevated levels of  $NO_x$  over the Arctic could thus be the cause of the 575 deviation of the bromine record from the MSA, sea ice proxy record.

The high correlation between the preindustrial (1750-1850 C.E.)  $NO_3^-$  and Br records (Fig. 9) supports this observation of co-transport and sink of Br and  $NO_3^-$  into the snow pack, though the natural sources of each are distinctly different. In the industrial era the low frequency temporal profile of the total bromine and nitrate records differ considerably, particularly at Summit (Fig. S15), apparently questioning the tight relationship observed before 1850. However, the positive correlation between the nitrate and the Br/MSA (Fig. 4) and nsiBr (Fig. 8) records is striking at both sites. The large relative increase in bromine (compared with MSA) during the era of high  $NO_x$  pollution may point to a non-sea

- ice source of bromine linked to nitrate emissions or simply an increased spring-time emission and summer-time deposition of Br from sea ice sources.
- Bromine and  $NO_r$  species shared a common source in the 20<sup>th</sup> century through the combustion of leaded 585 586 gasoline (Sect. 4.1.2). As discussed above, we observe that leaded fuel pollution reaching the Arctic 587 began to decline after 1970 in-line with reduced global consumption, but the amount of bromine inexcess of natural sources (nsiBr) continued to increase – following the trends in  $NO_x$  pollution (Fig. 588 8a). The continued increase in  $NO_x$  despite the decline in leaded fuel combustion is attributed primarily 589 to biomass burning, soil emissions and unleaded fossil fuel combustion (Lamarque et al., 2013). As the 590 leaded fuel source of bromine began to decline, organic bromine pollutants continued to increase, as 591 592 was discussed in Sect. 4.1.4. This can only account for a small fraction of the observed Br. The 593 continued correlation between nitrate and nsiBr despite the decoupling of nitrate and bromine 594 anthropogenic sources after 1970, suggests that nitrate pollution is likely influencing the processing of 595 local, natural sources of bromine in the polar MBL, in effect increasing the mobility of the bromine and thus its flux and preservation in the ice sheet. 596

#### 597 4.2.4 Consequences of nitrate driven increased bromine mobility in the Arctic

Plumes of BrO emitted from sea ice regions have been linked to mercury deposition events which lead to an increase in the bioavailability of toxic mercury species in polar waters (Parrella et al., 2012). Increased spring-time mobilization of bromine from the sea ice induced by anthropogenic nitrate could therefore increase the frequency and duration of these events and thus the mercury toxicity of the oceans. Increased atmospheric bromine concentrations would also increase the frequency of ozone depletion events (Simpson et al., 2007) thereby altering the oxidative chemistry of the polar MBL.

Whilst several studies have begun to explore bromine records from ice cores as a proxy for past sea ice conditions, the results of this study demonstrate that in an era of massive increases in atmospheric acidity the natural relationship between bromine and sea ice conditions can become distorted, precluding it from being an effective modern-day Arctic sea ice proxy.

708

### 709 **5** Conclusion

In this study we have shown that high resolution MSA measurements preserved in ice cores can be used as a proxy for sea ice conditions (specifically the size of the marginal sea ice zone) along specific sections of the Greenland coast. The MSA records show that sea ice began to decline at the end of the LIA and again, more dramatically during the Industrial period. Also, unsurprisingly, the changes in sea 24 714 ice conditions in the northern sites have been less dramatic than along the southern coastline. 715 Comparison between the 260 year records of bromine and MSA presented in this study allow us to show 716 that in the preindustrial era bromine concentrations preserved in the Greenland ice sheet are also likely 717 linked to the local sea ice conditions. With the decline of sea ice in the modern era and the dramatic 718 increase in acidic pollutants reaching the Arctic the sea ice-bromine connection is distorted, precluding 719 it from being an effective, direct sea ice proxy during the industrial era. The introduction of NOx 720 pollution in particular, into the clean Arctic environment promotes mobilization of bromine from the 721 sea ice, which in turn increases the bromine enrichment of the sea salt aerosols, forcing more bromine 722 inland (particularly in spring) than would occur naturally. Nitrate has also been linked with the 723 mechanism for preservation of bromine in the snowpack. The summer-time maximum of nitrate may 724 therefore be responsible for the observed summer-time bromine maximum preserved in the ice cores. 725 Whilst Northern Hemisphere pollution may prevent bromine from being an effective modern-day sea 726 ice proxy in the Arctic, in Antarctica the anthropogenic flux of nitrate species is thought to be small in comparison with natural sources (Wolff, 2013), leaving room for the possibility that bromine may still 727 be an effective proxy for local Antarctic sea ice conditions and for preindustrial sea ice reconstructions. 728

- 729
- 730

# 731 Author contribution

732 Manuscript written and data analysis performed by O.J.M with expert editing by E.S.. Ice cores supplied

by J.R.M.. Tunu ice core was collected and processed by O.J.M, J.R.M., N.J.C, M.S., R.H.R. under the
leadership of Beth Bergeron. Ice cores dated by M.S., J.R.M.. ICP-MS and CFA measurements

performed by O.J.M, J.R.M., N.J.C., L.L, D.P., M.S. MSA measurements designed and performed byM.G., E.S.

737

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#### 741 References

742 Abbatt, J., Oldridge, N., Symington, A., Chukalovskiy, V., McWhinney, R. D., Sjostedt, S. and Cox, R.

Comment [ojm1]: Change titles with CAPS and remove hyperlinks Comment [ojm2]:

- 743 A .: Release of gas-phase halogens by photolytic generation of OH in frozen halide-nitrate solutions: an

744 active halogen formation mechanism?, J. Phys. Chem. A, 114(23), 6527-33, doi:10.1021/jp102072t, 2010. 745

Abbatt, J. P. D.: Interactions of HBr, HCl, and HOBr With Supercooled Sulfuric- Acid-Solutions of 746 Stratospheric Composition, J. Geophys. Res., 100(D7), 14009-14017, 1995. 747

748 Abbatt, J. P. D., Thomas, J. L., Abrahamsson, K., Boxe, C., Granfors, A., Jones, A. E., King, M. D.,

Saiz-Lopez, A., Shepson, P. B., Sodeau, J., Toohey, D. W., Toubin, C., von Glasow, R., Wren, S. N. 749 750 and Yang, X .: Halogen activation via interactions with environmental ice and snow in the polar lower 751 troposphere and other regions, Atmos. Chem. Phys., 12(14), 6237-6271, doi:10.5194/acp-12-6237-

- 752 2012, 2012.
- 753 Abram, N. J., Wolff, E. W. and Curran, M. A. J.: A review of sea ice proxy information from polar ice 754 cores, Quat. Sci. Rev., 79, 168-183, doi:10.1016/j.quascirev.2013.01.011, 2013.

755 Appenzeller, C., Schwander, J., Sommer, S. and Stocker, T. F.: The North Atlantic Oscillation and its imprint on precipitation and ice accumulation in Greenland, Geophys. Res. Lett., 25(11), 1939, 756 757 doi:10.1029/98GL01227, 1998.

758 Arienzo, M. M., McConnell, J. R., Chellman, N., Criscitiello, A. S., Curran, M., Fritzsche, D., Kipfstuhl,

- S., Mulvaney, R., Nolan, M., Opel, T., Sigl, M. and Steffensen, J. P.: A Method for Continuous 239Pu 759 760 Determinations in Arctic and Antarctic Ice Cores, Environ. Sci. Technol., 50(13), 7066-7073, 761 doi:10.1021/acs.est.6b01108, 2016.
- 762 Barrie, L. A., Hoff, R. M. and Daggupaty, S. M.: The influence of mid-latitudinal pollution sources on haze in the Canadian arctic, Atmos. Environ., 15(8), 1407-1419, doi:10.1016/0004-6981(81)90347-4, 763 1981. 764
- 765 Berg, W. W., Sperry, P. D., Rahn, K. A. and Gladney, E. S.: Atmospheric Bromine in the Arctic, J. Geophys. Res., 88, 6719-6736, doi:10.1029/JC088iC11p06719, 1983. 766
- 767 Bertram, F. J. and Kolowich, J. B.: A study of methyl bromide emissions from automobiles burning
- 768 leaded gasoline using standardized vehicle testing procedures, Geophys. Res. Lett., 27(9), 1423–1426,
- doi:10.1029/1999GL011008, 2000. 769
- 770 Bowen, H. J. M.: Environmental chemistry of the elements / H. J. M. Bowen, BOOK, Academic Press,

- 771 London; New York., 1979.
- 772 Chellman, N. J., Hastings, M. G. and McConnell, J. R.: Increased nitrate and decreased  $\delta^{15}$ N–NO<sub>3</sub><sup>-</sup> in
- the Greenland Arctic after 1940 attributed to North American oil burning, Cryosph. Discuss., 1–22,
  doi:10.5194/tc-2016-163, 2016.
- Chen, Q. S., Bromwich, D. H. and Bai, L.: Precipitation over Greenland retrieved by a dynamic method
  and its relation to cyclonic activity, J. Clim., 10(5), 839–870, 1997.
- Chu, L. and Anastasio, C.: Formation of hydroxyl radical from the photolysis of frozen hydrogen
  peroxide, J. Phys. Chem. A, 109(28), 6264–6271, doi:10.1021/jp051415f, 2005.
- Curran, M. A. J. and Jones, G. B.: Dimethyl sulfide in the Southern Ocean: Seasonality and flux, J.
  Geophys. Res., 105(D16), 20451, doi:10.1029/2000JD900176, 2000.
- Curran, M. A. J., van Ommen, T. D., Morgan, V. I., Phillips, K. L. and Palmer, A. S.: Ice core evidence
  for Antarctic sea ice decline since the 1950s., Science, 302(5648), 1203–1206,
  doi:10.1126/science.1087888, 2003.
- Draxler, R. R. and Hess, G. D.: An Overview of the HYSPLIT\_4 Modelling System for Trajectories,
  Dispersion, and Deposition., Aust. Meteorol. Mag., 47(June 1997), 295–308, 1998.
- Fan, S.-M. and Jacob, D. J.: Surface ozone depletion in Arctic spring sustained by bromine reactions on
  aerosols, Nature, 359(6395), 522–524, doi:10.1038/359522a0, 1992.
- Felix, J. D. and Elliott, E. M.: The agricultural history of human-nitrogen interactions as recorded in ice
  core δ 15 N-NO3-, Geophys. Res. Lett., 40(8), 1642–1646, doi:10.1002/grl.50209, 2013.
- Finlayson-Pitts, B. J.: The Tropospheric Chemistry of Sea Salt: A Molecular-Level View of the
  Chemistry of NaCl and NaBr, Chem. Rev., 103(12), 4801–4822, doi:10.1021/cr020653t, 2003.
- Fischer, H. and Wagenbach, D.: Large-scale spatial trends in recent firn chemistry along an east-west
  transect through central Greenland, Atmos. Environ., 30(19), 3227–3238, doi:10.1016/1352-
- 794 2310(96)00092-1, 1996.
- Frinak, E. K. and Abbatt, J. P. D.: Br2 production from the heterogeneous reaction of gas-phase OH
  with aqueous salt solutions: Impacts of acidity, halide concentration, and organic surfactants., J. Phys.
  Chem. A, 110(35), 10456–64, doi:10.1021/jp0631650, 2006.
- George, I. J. and Anastasio, C.: Release of gaseous bromine from the photolysis of nitrate and hydrogen
  peroxide in simulated sea-salt solutions, Atmos. Environ., 41(3), 543–553,
  doi:10.1016/j.atmosenv.2006.08.022, 2007.

- Hunke, E. C., Notz, D., Turner, A. K. and Vancoppenolle, M.: The multiphase physics of sea ice: a
  review for model developers, Cryosph., 5(4), 989–1009, doi:10.5194/tc-5-989-2011, 2011.
- 303 Jacobi, H. W., Kleffmann, J., Villena, G., Wiesen, P., King, M., France, J., Anastasio, C. and Staebler,
- R.: Role of nitrite in the photochemical formation of radicals in the snow, Environ. Sci. Technol., 48(1),
  165–172, doi:10.1021/es404002c, 2014.
- Jaffrezo, J. L., Davidson, C. I., Legrand, M. and Dibb, J. E.: Sulfate and MSA in the air and snow on the Greenland Ice Sheet, J. Geophys. Res., 99(D1), 1241–1253, doi:10.1029/93JD02913, 1994.
- Kahl, J. D. W., Martinez, D. A., Kuhns, H., Davidson, C. I., Jafferezo, J. L. and Harris, J. M.: Air mass
  trajectories to Summit, Greenland : A 44-year climatology and some episodic events, J. Geophys. Res.
  Ocean., 102(C12), 26861–26875, 1997.
- Kerkweg, A., Jöckel, P., Warwick, N., Gebhardt, S., Brenninkmeijer, C. A. M. and Lelieveld, J.:
  Consistent simulation of bromine chemistry from the marine boundary layer to the stratosphere Part
- 313 2: Bromocarbons, Atmos. Chem. Phys. Discuss., 8(3), 9477–9530, doi:10.5194/acpd-8-9477-2008,
  314 2008.
- Kinnard, C., Zdanowicz, C. M., Koerner, R. M. and Fisher, D. A.: A changing Arctic seasonal ice zone:
  Observations from 1870-2003 and possible oceanographic consequences, Geophys. Res. Lett., 35(2),
- 317 2-6, doi:10.1029/2007GL032507, 2008.
- 318 Lamarque, J.-F., Dentener, F., McConnell, J., Ro, C.-U., Shaw, M., Vet, R., Bergmann, D., Cameron-
- 319 Smith, P., Dalsoren, S., Doherty, R., Faluvegi, G., Ghan, S. J., Josse, B., Lee, Y. H., MacKenzie, I. A.,
- 320 Plummer, D., Shindell, D. T., Skeie, R. B., Stevenson, D. S., Strode, S., Zeng, G., Curran, M., Dahl-
- 321 Jensen, D., Das, S., Fritzsche, D. and Nolan, M.: Multi-model mean nitrogen and sulfur deposition from
- the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): evaluation of historical and projected future changes, Atmos. Chem. Phys., 13(16), 7997–8018, doi:10.5194/acp-13-
- 324 7997-2013, 2013.
- Langendörfer, U., Lehrer, E., Wagenbach, D. and Platt, U.: Observation of filterable bromine
  variabilities during Arctic tropospheric ozone depletion events in high (1 hour) time resolution, J.
  Atmos. Chem., 34(1), 39–54, doi:10.1023/A:1006217001008, 1999.
- 328 Legrand, M., Hammer, C., De Angelis, M., Savarino, J., Delmas, R., Clausen, H. and Johnsen, S. J.:
- 329 Sulfur-containing species (methanesulfonate and SO4 ) over the last climatic cycle in the Greenland Ice
- Core Project (central Greenland) ice core, J. Geophys. Res., 102(C12), 26663, doi:10.1029/97JC01436,
  1997.
  - 29

- Lehrer, E., Wagenbach, D. and Platt, U.: Aerosol chemical composition during tropospheric ozone
  depletion at Ny Ålesund/Svalbard, Tellus B, 49(5), doi:10.3402/tellusb.v49i5.15987, 1997.
- Leu, E., Mundy, C. J., Assmy, P., Campbell, K., Gabrielsen, T. M., Gosselin, M., Juul-Pedersen, T. and
- Gradinger, R.: Arctic spring awakening Steering principles behind the phenology of vernal ice algal
  blooms, Prog. Oceanogr., 139, 151–170, doi:10.1016/j.pocean.2015.07.012, 2015.
- Li, S.-M. and Barrie, L. A.: Biogenic sulfur aerosol in the Arctic troposphere: 1. Contributions to total
  sulfate, J. Geophys. Res., 98(D11), 20613, doi:10.1029/93JD02234, 1993.
- Macias Fauria, M., Grinsted, A., Helama, S., Moore, J., Timonen, M., Martma, T., Isaksson, E. and
  Eronen, M.: Unprecedented low twentieth century winter sea ice extent in the Western Nordic Seas
  since A.D. 1200, Clim. Dyn., 34(6), 781–795, doi:10.1007/s00382-009-0610-z, 2010.
- Mann, M. E., Bradley, R. S. and Hughes, M. K.: Global-scale temperature patterns and climate forcing
  over the past six centuries, Nature, 392(6678), 779–787, doi:10.1038/33859, 1998.
- Maselli, O. J., Fritzsche, D., Layman, L., McConnell, J. R. and Meyer, H.: Comparison of water isotoperatio determinations using two cavity ring-down instruments and classical mass spectrometry in
  continuous ice-core analysis., Isotopes Environ. Health Stud., 49(September 2014), 387–98,
  doi:10.1080/10256016.2013.781598, 2013.
- McConnell, J. R. and Edwards, R.: Coal burning leaves toxic heavy metal legacy in the Arctic., Proc.
  Natl. Acad. Sci. U. S. A., 105(34), 12140–12144, doi:10.1073/pnas.0803564105, 2008.
- McConnell, J. R., Lamorey, G. W., Lambert, S. W. and Taylor, K. C.: Continuous ice-core chemical
  analyses using inductively coupled plasma mass spectrometry., Environ. Sci. Technol., 36(775), 7–11,
  doi:10.1021/es011088z, 2002.
- 353 McConnell, J. R., Edwards, R., Kok, G. L., Flanner, M. G., Zender, C. S., Saltzman, E. S., Banta, J. R.,
- 354 Pasteris, D. R., Carter, M. M. and Kahl, J. D. W.: 20th-Century Industrial Black Carbon Emissions
- 355 Altered Arctic Climate Forcing, Science, 317, 1381–1384, doi:10.1126/science.1144856, 2007.
- Millero, F. J.: The Physical Chemistry of Seawater, Annu. Rev. Earth Planet. Sci., 2(1), 101–150,
   doi:10.1146/annurev.ea.02.050174.000533, 1974.
- Moldanová, J. and Ljungström, E.: Sea-salt aerosol chemistry in coastal areas: A model study, J.
  Geophys. Res., 106, 1271, doi:10.1029/2000JD900462, 2001.
- 360 Montzka, S. and Reimann, S.: Scientific Assessment of Ozone Depletion 2010: Scientific Summary
- 361 Chapter 1 Ozone-Depleting Substances (ODSs) and Related Chemicals. [online] Available from:
  - 30

- http://www.esrl.noaa.gov/csd/assessments/ozone/2010/summary/ch1.html (Accessed 23 December
   2015), 2010.
- Morin, S., Savarino, J., Frey, M. M., Yan, N., Bekki, S., Bottenheim, J. and Martins, J. M. F.: Tracing
  the origin and fate of NOx in the Arctic atmosphere using stable isotopes in nitrate., Science, 322(5902),
  730–2, doi:10.1126/science.1161910, 2008.
- Mulvaney, R., Pasteur, E. C., Peel, D. A., Saltzman, E. S. and Whung, P.-Y.: The ratio of MSA to nonsea-salt sulphate in Antarctic Peninsula ice cores, Tellus B, 44(4), doi:10.3402/tellusb.v44i4.15457,
  1992.
- Nghiem, S. V., Rigor, I. G., Richter, A., Burrows, J. P., Shepson, P. B., Bottenheim, J., Barber, D. G.,
  Steffen, A., Latonas, J., Wang, F., Stern, G., Clemente-Colón, P., Martin, S., Hall, D. K., Kaleschke, L.,
- Tackett, P., Neumann, G. and Asplin, M. G.: Field and satellite observations of the formation and
   distribution of Arctic atmospheric bromine above a rejuvenated sea ice cover, J. Geophys. Res. Atmos.,
- 374 117(D17), n/a-n/a, doi:10.1029/2011JD016268, 2012.
- Nriagu, J. O.: The rise and fall of leaded gasoline, Sci. Total Environ., 92, 13–28, 1990.
- NSIDC, National Snow and Ice Data Center, [online] Available from:
  http://nsidc.org/cryosphere/seaice/data/terminology.html (Accessed December 2013).
- O'Dwyer, J., Isaksson, E., Vinje, T., Jauhiainen, T., Moore, J., Pohjola, V., Vaikmae, R. and van de
  Wal, R. S. W.: Methanesulfonic acid in a Svalbard ice core as an indicator of ocean climate, Geophys.
- Res. Lett., 27(8), 1159–1162, doi:10.1029/1999GL011106, 2000.
- Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G.,
  Brasseur, G. and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model:
- description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys., 12(3), 1423–1447,
  doi:10.5194/acp-12-1423-2012, 2012.
- Oudijk, G.: The Rise and Fall of Organometallic Additives in Automotive Gasoline, Environ. Forensics,
  11(933126918), 17–49, doi:10.1080/15275920903346794, 2010.
- 387 Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., Evans, M. J., Yang, X., Pyle,
- J. A., Theys, N. and Van Roozendael, M.: Tropospheric bromine chemistry: implications for present
  and pre-industrial ozone and mercury, Atmos. Chem. Phys., 12(15), 6723–6740, doi:10.5194/acp-126723-2012, 2012.
- 391 Pasteris, D. R., McConnell, J. R. and Edwards, R.: High-resolution, continuous method for measurement
  - 31

- 392 of acidity in ice cores, Environ. Sci. Technol., 46, 1659–1666, doi:10.1021/es202668n, 2012.
- Pratt, K. A., Custard, K. D., Shepson, P. B., Douglas, T. A., Pöhler, D., General, S., Zielcke, J., Simpson,
- W. R., Platt, U., Tanner, D. J., Gregory Huey, L., Carlsen, M. and Stirm, B. H.: Photochemical
  production of molecular bromine in Arctic surface snowpacks, Nat. Geosci., 6(5), 351–356,
  doi:10.1038/ngeo1779, 2013.
- Rankin, A. M., Wolff, E. W. and Martin, S.: Frost flowers: Implications for tropospheric chemistry and
  ice core interpretation, J. Geophys. Res. Atmos., 107(D23), 4683, doi:10.1029/2002JD002492, 2002.
- Rayner, N. A.: Global analyses of sea surface temperature, sea ice, and night marine air temperature
   since the late nineteenth century, J. Geophys. Res., 108(D14), 4407, doi:10.1029/2002JD002670, 2003.
- 301 Röthlisberger, R., Bigler, M., Hutterli, M., Sommer, S., Stauffer, B., Junghans, H. G. and Wagenbach,
- 902
   D.: Technique for continuous high-resolution analysis of trace substances in firn and ice cores, Environ.
- 903
   Sci. Technol., 34(2), 338–342, doi:10.1021/es9907055, 2000.
- Röthlisberger, R., Mulvaney, R., Wolff, E. W., Hutterli, M. a., Bigler, M., Sommer, S. and Jouzel, J.:
  Dust and sea salt variability in central East Antarctica (Dome C) over the last 45 kyrs and its implications
  for southern high-latitude climate, Geophys. Res. Lett., 29(20), 1–4, doi:10.1029/2003GL016936, 2002.
- Saltzman, E. S., Dioumaeva, I. and Finley, B. D.: Glacial/interglacial variations in methanesulfonate
  (MSA) in the Siple Dome ice core, West Antarctica, Geophys. Res. Lett., 33(11), 1–4,
  doi:10.1029/2005GL025629, 2006.
- Sander, R., Rudich, Y., von Glasow, R. and Crutzen, P. J.: The role of BrNO3 in marine tropospheric
  chemistry: A model study, Geophys. Res. Lett., 26(18), 2857–2860, doi:10.1029/1999GL900478, 1999.
- 312 Sander, R., Keene, W. C., Pszenny, A. A. P., Arimoto, R., Ayers, G. P., Baboukas, E., Cainey, J. M.,
- 13 Crutzen, P. J., Duce, R. A., Hönninger, G., Huebert, B. J., Maen-haut, W., Mihalopoulos, N., Turekian,
- 914 V. C. and Van Dingenen, R.: Inorganic bromine in the marine boundary layer: a critical review, Atmos.
- 315 Chem. Phys., 3, 1301–1336, doi:10.5194/acp-3-1301-2003, 2003.
- 316 Schönhardt, A., Begoin, M., Richter, A., Wittrock, F., Kaleschke, L., Gómez Martín, J. C. and Burrows,
- 317 J. P.: Simultaneous satellite observations of IO and BrO over Antarctica, Atmos. Chem. Phys., 12(14),
- 918 6565-6580, doi:10.5194/acp-12-6565-2012, 2012.
- 319 Sharma, S., Chan, E., Ishizawa, M., Toom-Sauntry, D., Gong, S. L., Li, S. M., Tarasick, D. W., Leaitch,
- 20 W. R., Norman, A., Quinn, P. K., Bates, T. S., Levasseur, M., Barrie, L. A. and Maenhaut, W.: Influence
- 321 of transport and ocean ice extent on biogenic aerosol sulfur in the Arctic atmosphere, J. Geophys. Res.
  - 32

- 922 Atmos., 117(12), n/a-n/a, doi:10.1029/2011JD017074, 2012.
- 323 Sigl, M., McConnell, J. R., Layman, L., Maselli, O. J., McGwire, K., Pasteris, D., Dahl-Jensen, D.,
- Steffensen, J. P., Vinther, B., Edwards, R., Mulvaney, R. and Kipfstuhl, S.: A new bipolar ice core
  record of volcanism from WAIS Divide and NEEM and implications for climate forcing of the last 2000
  years, J. Geophys. Res. Atmos., 118(3), 1151–1169, doi:10.1029/2012JD018603, 2013.
- 327 Sigl, M., Winstrup, M., McConnell, J. R., Welten, K. C., Plunkett, G., Ludlow, F., Büntgen, U., Caffee,
- 328 M., Chellman, N., Dahl-Jensen, D., Fischer, H., Kipfstuhl, S., Kostick, C., Maselli, O. J., Mekhaldi, F.,
- 329 Mulvaney, R., Muscheler, R., Pasteris, D. R., Pilcher, J. R., Salzer, M., Schüpbach, S., Steffensen, J. P.,
- 30 Vinther, B. M. and Woodruff, T. E.: Timing and climate forcing of volcanic eruptions for the past 2,500
- 931 years, Nature, 523(7562), 543–9, doi:10.1038/nature14565, 2015.
- 32 Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J.,
- 33 Carpenter, L. J., Friess, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L., Neff,
- B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner,
  T. and Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, 4375–4418,
- 436 doi:10.5194/acpd-7-4285-2007, 2007.
- 37 Sjostedt, S. J., Huey, L. G., Tanner, D. J., Peischl, J., Chen, G., Dibb, J. E., Lefer, B., Hutterli, M. A.,
  38 Beyersdorf, A. J., Blake, N. J., Blake, D. R., Sueper, D., Ryerson, T., Burkhart, J. and Stohl, A.:
  39 Observations of hydroxyl and the sum of peroxy radicals at Summit, Greenland during summer 2003,
  340 Atmos. Environ., 41(24), 5122–5137, doi:10.1016/j.atmosenv.2006.06.065, 2007.
- Smith, S. J., van Aardenne, J., Klimont, Z., Andres, R. J., Volke, A. and Delgado Arias, S.:
  Anthropogenic sulfur dioxide emissions: 1850–2005, Atmos. Chem. Phys., 11(3), 1101–1116,
  doi:10.5194/acp-11-1101-2011, 2011.
- 944 Spolaor, A., Vallelonga, P., Plane, J. M. C., Kehrwald, N., Gabrieli, J., Varin, C., Turetta, C., Cozzi, G.,
- Kumar, R., Boutron, C. and Barbante, C.: Halogen species record Antarctic sea ice extent over glacialinterglacial periods, Atmos. Chem. Phys., 13, 6623–6635, doi:10.5194/acp-13-6623-2013, 2013a.
- 347 Spolaor, A., Gabrieli, J., Martma, T., Kohler, J., Björkman, M. B., Isaksson, E., Varin, C., Vallelonga,
- )48 P., Plane, J. M. C. and Barbante, C.: Sea ice dynamics influence halogen deposition to Svalbard,
- <sup>3</sup>49 Cryosph., 7(5), 1645–1658, doi:10.5194/tc-7-1645-2013, 2013b.
- 50 Spolaor, A., Vallelonga, P., Gabrieli, J., Martma, T., Björkman, M. P., Isaksson, E., Cozzi, G., Turetta,
- 951 C., Kjær, H. A., Curran, M. A. J., Moy, A. D., Schönhardt, A., Blechschmidt, A.-M., Burrows, J. P.,
- 952 Plane, J. M. C. and Barbante, C.: Seasonality of halogen deposition in polar snow and ice, Atmos. Chem.
  - 33

- 953 Phys., 14(18), 9613–9622, doi:10.5194/acp-14-9613-2014, 2014.
- 954 Spolaor, A., Opel, T., McConnell, J. R., Maselli, O. J., Spreen, G., Varin, C., Kirchgeorg, T., Fritzsche,
- 955 D., Saiz-Lopez, A. and Vallelonga, P.: Halogen-based reconstruction of Russian Arctic sea ice area
- from the Akademii Nauk ice core (Severnaya Zemlya), Cryosph., 10, 245–256, doi:10.5194/tcd-9-44072015, 2016.
- Sturges, W. T. and Harrison, R. M.: Bromine:Lead ratios in airborne particles from urban and rural sites,
   Atmos. Environ., 20(3), 577–588, doi:10.1016/0004-6981(86)90101-0, 1986.
- Thomas, J. L., Dibb, J. E., Huey, L. G., Liao, J., Tanner, D., Lefer, B., von Glasow, R. and Stutz, J.:
  Modeling chemistry in and above snow at Summit, Greenland Part 2: Impact of snowpack chemistry
  on the oxidation capacity of the boundary layer, Atmos. Chem. Phys., 12(14), 6537–6554,
  doi:10.5194/acp-12-6537-2012, 2012.
- 764 Thomas, V. M., Bedford, J. A. and Cicerone, R. J.: Bromine emissions from leaded gasoline, Geophys.
  765 Res. Lett., 24(11), 1371–1374, doi:10.1029/97GL01243, 1997.
- 966 Vestreng, V., Ntziachristos, L., Semb, A., Reis, S., Isaksen, I. S. A. and Tarrasón, L.: Evolution of NO<sub>x</sub>
- emissions in Europe with focus on road transport control measures, Atmos. Chem. Phys., 9(4), 1503–
  1520, doi:10.5194/acp-9-1503-2009, 2009.
- Wagner, T., Leue, C., Wenig, M., Pfeilsticker, K. and Platt, U.: Spatial and temporal distribution of
  enhanced boundary layer BrO concentrations measured by the GOME instrument aboard ERS-2, J.
  Geophys. Res., 106(D20), 24225, doi:10.1029/2000JD000201, 2001.
- Wais Divide Project Memebers: Onset of deglacial warming in West Antarctica driven by local orbital
  forcing., Nature, 500(7463), 440–4, doi:10.1038/nature12376, 2013.
- 974 Walsh, J. E.: A data set on Northern Hemisphere sea ice extent, Natl. Snow Ice Data Cent., 49–51, 1978.
- 75 Weißbach, S., Wegner, A., Opel, T., Oerter, H., Vinther, B. M. and Kipfstuhl, S.: Spatial and temporal
- oxygen isotope variability in northern Greenland implications for a new climate record over the past
  millennium, Clim. Past Discuss., 11(3), 2341–2388, doi:10.5194/cpd-11-2341-2015, 2015.
- 978 Weller, R.: Postdepositional losses of methane sulfonate, nitrate, and chloride at the European Project
- 979 for Ice Coring in Antarctica deep-drilling site in Dronning Maud Land, Antarctica, J. Geophys. Res.,
- 980 109(D7), 1-9, doi:10.1029/2003JD004189, 2004.
- 981 WMO: Scientific Assessment of Ozone Depletion: 1994. Chapter 10: Methyl Bromide, Geneva., 1995.
- 982 WMO: Scientific Assessment of Ozone Depletion: 2002. Chapter 1: Controlled Substances and Other

- 383 Source Gases., 2002.
- Wolff, E. W.: Ice sheets and nitrogen, Philos. Trans. R. Soc. Lond. B. Biol. Sci., 368,
  doi:10.1098/rstb.2013.0127, 2013.
- Wolff, E. W., Rankin, A. M. and Röthlisberger, R.: An ice core indicator of Antarctic sea ice
  production?, Geophys. Res. Lett., 30(22), 2–5, doi:10.1029/2003GL018454, 2003.
- Xu, L., Russell, L. M., Somerville, R. C. J. and Quinn, P. K.: Frost flower aerosol effects on Arctic
  wintertime longwave cloud radiative forcing, J. Geophys. Res. Atmos., 118(23), 13282–13291,
  doi:10.1002/2013JD020554, 2013.
- Yang, X., Pyle, J. A. and Cox, R. A.: Sea salt aerosol production and bromine release: Role of snow on
  sea ice, Geophys. Res. Lett., 35(16), 1–5, doi:10.1029/2008GL034536, 2008.
- Yang, X., Pyle, J. A., Cox, R. A., Theys, N. and Van Roozendael, M.: Snow-sourced bromine and its
  implications for polar tropospheric ozone, Atmos. Chem. Phys., 10(16), 7763–7773, doi:10.5194/acp10-7763-2010, 2010.
- Yung, Y. L., Pinto, J. P., Watson, R. T. and Sander, S. P.: Atmospheric Bromine and Ozone
  Perturbations in the Lower Stratosphere, J. Atmos. Sci., 37(2), 339–353, doi:10.1175/15200469(1980)037<0339:ABAOPI>2.0.CO;2, 1980.
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Figure 1. Locations of ice cores used in this study. Summit-2010: (72°20'N 38°17'24"W), Tunu: (78°
2' 5.5"N, 33° 52' 48"W)

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Figure 2. Annual record of bromine (thin blue) and MSA (thin red). Annual record of bromine (thick blue) and MSA (thick red) with outlying spikes removed using a 25 year running average filter described by Sigl et al. (2013). All records were fit with a 3 step linear regression (black) and the results of the fits which identify the timing of inflection points are summarized in Table S1. The time-series have been plotted to match the signal variability in the preindustrial era (1750-1850 C.E.).

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)17 Figure 3. Upper plots: Average seasonal cycle of species in the Summit-2010 ice core. The left-hand Y )18 axes are associated with the solid lines, and the right-hand Y axes associated with the dashed lines. )19 Dashed lines (a-e): Average seasonal cycle from depths 43.5 - 87.3 m (years 1742-1900). Solid lines )20 (a-e): Average seasonal cycle from 0-43.5 m (years 1900-2010). Error bars indicate the standard error )21 of the monthly value. (a) Total bromine, (b) total sodium, (c) MSA, (d) nitrate. Units for (a-d) are nM. )22 Note that the seasonal cycle in bromine appears to broaden in the 1900-2010 period (see lower panel). )23 Note also that the MSA maximum shifts from spring in the shallowest part of the ice core (solid line) to )24 winter in the deepest part of the ice core (dashed line) due to post-depositional effects (see Fig. S1). (e)

- )25 Average seasonal cycle in bromine enrichment (relative to sea salt sodium, see Eq. (4)). (f-right) The
- block sea ice extent (SIE,  $x10^6$  km<sup>2</sup>) within an area of the East Greenland coast [70°- 63° N, 15°- 45° W], (f
- 127 left) Area of open water within the sea ice pack (OWIP,  $x10^6 \text{ km}^2$ ) for the area defined by SIE. (g-
- 128 left) Solar insolation at 12 GMT at the latitude of Summit (eosweb.larc.nasa.gov). (g-right) Annual
- )29 cycle of the  $\delta^{18}$ O water signal averaged over 1900-2010 C.E. Lower plot: Broadening of bromine
- 30 seasonal cycle in the Summit-2010 ice core. The difference between the summer and spring bromine
- 31 signal (JJA-MAM) was monitored over the length of the entire ice core. In the preindustrial era (pre-
- 1850) bromine peaks in summer; realised as positive values of JJA-MAM. After 1900 there is a marked
- broadening of the seasonal signal towards spring and by ~1970 the seasonal signal maximum is routinely
- 34 shared between summer and spring realised as an averaged JJA-MAM of approximately zero.
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)38 Figure 4. Comparison between the measured total sulfur (shown as sulfate) and acidity records from each ice core (top panels). The acidity record is dominated by the influence of the sulfur species until )39 )40 the early 21<sup>th</sup> century when the NO<sub>x</sub> pollution remains elevated whilst anthropogenic sulfur sources are depleted resulting in a slight relative elevation of the total acidity relative to total sulfur concentrations. )41 The large spikes in the acidity and sulfur records are identified as volcanic events. The ice core records )42 )43 cover the period of the 1783 Laki eruption as well as the Unknown 1909 eruption and Tambora eruption (Indonesia) in 1815 (Sigl et al., 2013). Comparison between Br/MSA and total acidity (center panels) )44 and nitrate  $(NO_3^-)$ , bottom panels) measured in the ice cores. The Br/MSA ratio follows the total acidity )45 )46 record closely except where the record is dominated by the sulfur component (e.g. early 1900s). Of the two major acidic species the Br/MSA follows the nitrate most closely at both ice core sites. )47

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)53 Figure 5. Air mass back trajectories from the (a) Summit-2010 and (b) Tunu ice core sites over the )54 period 2005-2013 C.E. Maps display the fraction of the total number of trajectory hours (ranging )55 between 21400-25500 hr month<sup>-1</sup>) spent at altitudes under 500 m. Back trajectories were allowed to travel for 10 days. New trajectories were started every 12 hours. Map grid resolution is 2°x 2°. Ice core )56 )57 locations are shown by a pink circle. Maps show that air masses consistently arrive at Summit from the SE Greenland coast with a smaller contribution from the SW coast. Air masses consistently arrive at )58 )59 Tunu from the western Greenland coast with a smaller contribution from the SE and NE coast. The air )60 mass originating from the NE coast is most dominant in May and comparison with the total vertical column profile (Fig. S8) shows it is confined to lower altitudes unlike those from the west coast. )61



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)65 Figure 6. Upper plot: Correlation map of monthly sea ice concentration (SIC) derived from the Summit-)66 )67 2010 ice core. The SIC map displayed corresponds to the month which shows the highest OWIP correlation (lower plot) with the annual MSA. Other monthly maps are shown in Fig. S9. (a) HadISST1 )68 )69 ICE dataset from 1900-2010 C.E. correlated with annual records of MSA (with outlier removed). Only )70 locations that showed a SIC variability greater than 10% and have a significant correlation (t-test, )71 p < 0.05) are displayed. The area of sea ice that is the likely source of MSA (as indicated by the air mass )72 trajectories) are outlined in black  $[70^{\circ}-63^{\circ}N, 0^{\circ}-45^{\circ}W]$ . (b) As for (a) but focused on the satellite )73 period 1979-2010 C.E. Lower plots: The correlation between the area of Open Water within the Ice )74 Pack (OWIP) calculated within the black outlined areas shown on the upper maps and the annual MSA )75 records (red, outliers removed - orange, nM). Summit-2010 MSA shows a significant, positive )76 correlation with the amount of OWIP during spring within the integrated regions over both time periods. The highest correlations were found for March over the 1979-2010 period and May for the 1900-2010 )77 )78 period. In (b) if the MSA source region is enlarged to [70°-63°N, 0°-60°W] the March OWIP/MSA )79 correlation increases slightly (from 0.38 to 0.4). The Summit-2010 enrBr(Na) (nM) and nsiBr (nM) records are also compared to the same OWIP records. Particularly over the longer time period there is )80 )81 little correlation between the series.



Figure 7. Upper plots: Correlation maps of monthly sea ice concentration (SIC) derived from the Tunu )87 )88 ice core. (a) HadISST1 ICE dataset from 1900-2012 C.E. correlated with annual records of MSA. The )89 monthly SIC map displayed corresponds to the month which shows the highest OWIP correlation (lower plot) with the annual MSA. Other monthly maps are shown in Fig. S10. Only locations that showed a )90 )91 SIC variability greater than 10% and have a significant correlation (t-test, p<0.05) are displayed. The )92 area of sea ice that is the likely source of MSA (as indicated by the air mass trajectories) are outlined in )93 black [77°- 67°N, 62°-50°W]. (b) As for (a) but focused on the satellite period 1979-2012 C.E. Lower )94 plots: The correlation between the area of Open Water within the Ice Pack (OWIP) calculated within )95 the black outlined areas shown on the upper maps and the annual MSA records (red, outliers removed -)96 orange). The Tunu enrBr(Na) (nM) and nsiBr (nM) records are also compared to the same OWIP )97 records and show poor correlation, particulary over the longer time period. )98







103 Figure 8. Upper panels: Comparison between bromine in excess of what is expected from a purely sea 104 ice source (nsiBr, black) and nitrate. The temporal similarities between the nitrate and nsiBr records are 105 high and indicate that nitrate is a likely driving force for the enhanced release of bromine species from sea ice sources. Lower panels: Comparison between the calculated nsiBr record and excess lead (exPb, 106 107 purple) measured in the ice cores. The lower panels also show the upper limit to the amount of bromine 108 that could be derived from leaded fuel combustion by assuming exPb:Br ratio of 1:2 after 1925 (blue). After 1970, when world consumption of leaded gasoline began to fall, nsiBr concentrations continued 109 110 to rise at both ice core sites far above the concentrations that could be explained by leaded gasoline 111 sources.

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Figure 9. High frequency comparison between the annual bromine, nitrate and sulfate records measured 117 118 in the ice cores. Each series has been detrended with an 11 year running average before comparison to 119 remove the low frequency changes in each record. The correlation is highest between bromine and nitrate at both sites. The r-value for bromine versus nitrate at Summit increases in significance (r=0.24, 120 121 p=0.001) when the entire period (1750-2010) is considered. At both sites there is a close relationship 122 between the variability in the nitrate and bromine due to their intimate relationship during emission 123 from the sea ice, transport and deposition onto the snow pack. The correlation between sulfate (or indeed 124 bulk acidity) and bromine is not significant over any of the time periods shown at either site. Particularly

- 125 evident is the non-response of the bromine signal to the sulfur rich volcanic events as described in
- 126 Sect.4.2.2.
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# Supplementary figures and tables

- 2 Table S1. Summary of timings of each inflection in the 3-step linear regression of annual bromine and MSA
- 3 at Summit and Tunu. Regression was performed on the data sets with outliers removed as described in Fig. 2.
- 4 The signs indicate the direction of the inflection in the record, errors are  $2\sigma$ .

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# Timing of inflection (Year, C.E.)

	Infl. 1		Infl. 2		Infl. 3		Infl. 4
	Br	MSA	Br	MSA	Br	MSA	Br
Summit- 2010	(-)1819 ±22	(-)1854 ±12	(+)1879 ±22	(+)1878 ±12	(+)1932 ±10	(-)1930 ±16	(-)1974 ±20
Tunu	(-)1842 ±22	(-)1812 ±12	(+)1857 ±24	(+)1821 ±21	(+)1944 ±18	(-)1984 ±4	(+)1966 ±20

- 1 Table S2. Summary of the average aerosol concentrations as determined by the 3-step linear regression of
- 2 annual bromine and MSA at Summit and Tunu displayed in Fig. 2. The duration of each step in concentration
- 3 is bracketed by the inflection points summarized in Table S1. Concentrations are in units of nM. MSA did not
- 4 show a stable period after the third infection in the series and so was not assigned a concentration value for
- 5 'Step 3'. Errors represent  $2\sigma$  in the concentration value.
- 6

#### Concentration (nM)

	Step 1		Step 2	Step 3	
	Br	MSA	Br	MSA	Br
Summit-2010	5.4±0.2	48±1	4.2±0.2	36±2	5.5±0.3
Tunu	4.2±0.3	25±1	3.2±0.3	21.2±0.7	4.8±0.5



Figure S1. Illustration of the shift in the seasonal MSA peak along the length of the Summit-2010 ice core.
The difference in amplitude between the spring/summer and winter/fall MSA signal each year was calculated ((MAM+JJA)-(DJF+SON)) and observed to shift linearly along the length of the ice core. At the shallowest,
part of the ice core the positive values show the MSA peak appears in the spring/summer whilst in the deepest and oldest part of the ice core the signal has shifted to a winter/fall annual maximum. This phenomenon has previously been attributed to annual salt gradients within the ice core driving the migration of the MSA toward the higher salt location, winter (Mulvaney et al., 1992; Weller, 2004).





Figure S2. Comparison between the annual cycle in inorganic Br measured at Summit from snow samples
taken as part of the GEOSummit project (2007-2013) and in the Summit-2010 ice core (1900-2010). The snow
samples were analysed for inorganic Br on the same system used to measure the ice core records. The results
of the snow samples support the observation from the ice cores that the maximum flux of Br is in summer
with a possible secondary peak in spring. The error bars represent 1σ.



Figure S3. Monthly values of bromine, sodium and chlorine compared with their sea water ratio (red). At
both sites, both the Br/Na and Br/Cl lie predominantly above the sea water ratio, whilst Cl/Na shows only a
small Cl enrichment which increases at small sodium concentrations. At Tunu, 11% and 12% of the points
show bromine depletion relative to Na and Cl, respectively. ([Br]/[Na])<sub>seawater</sub> = 1.793x10<sup>-3</sup>,
([Br]/[Cl])<sub>seawater</sub> = 1.539x10<sup>-3</sup>. ([Cl]/[Na])<sub>seawater</sub> = 1.165



2 Figure S4. Total bromine and bromine enrichment (relative to sodium) from the Summit-2010 ice core.



1 2 3 Figure S5. Comparison between the MSA record obtained from the GRIP ice core (Legrand et al., 1997) in 4 1993 and the Summit-2010 ice core from this study. The Summit-2010 ice core drill-site (72°20'N 5 38°17'24"W) is located 35 km SW of the GRIP ice core drill-site (72°34'N, 37°38'W). The GRIP MSA was 6 measured in discrete samples using ion chromatography compared with the Summit-2010 ice core which was 7 measured using the new technique of continuous melting of the ice core combined with continuous analysis 8 by electrospray triple-quad mass spectrometry (as described in the text). The tight overlap between low 9 frequency trend of the two series demonstrates that the new, continuous measurement technique is able to 10 achieve a comparable accuracy in MSA concentration measurements to the discrete technique. It also 11 demonstrates that negligible amounts of MSA are being lost during the continuous melt method. Discrepancies 12 between the high frequency features of the two records is expected as the measurement resolution of the 13 continuous method is much higher than the discrete method and the two records are from different ice core 14 sites.



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Figure S6. Demonstration of the reproducibility of the MSA online, continuous measurements performed on the Tunu ice core. Two different depths of the Tunu ice core are shown where the replicate analysis was performed by melting a secondary stick of ice cut from the same ice core and overlapping in depth ('overlap' ice sticks) : (a) Six 'overlap' ice sticks were melted sequentially to replicate the MSA record over the depth 8-14 m.(b) Two 'overlap' ice sticks were melted sequentially over the depth 186.2-187.9 m. Zooming in on a small section of the record at each depth demonstrates that the high frequency signal is real (not noise) and well replicated by the continuous MSA technique.



1 2 Figure S7. Comparison between discrete and continuous, online measurements of MSA measurements from 3 the Tunu ice core samples. The discrete samples were collected as the continuous measurements were 4 performed by directing part of the sample stream into an auto-sampler collection system just before they 5 entered the analyzer. The samples were then frozen and later measured using ion chromatographic separation and the ESI/MS/MS detection. In this plot the continuous data have been averaged over the same depth range 6 7 covered by each discrete sample and then both series plotted as the average age over that depth range. Over 8 the 1750-2012 period the Tunu discrete measurements were, on average, 7% higher than the online 9 measurements (dashed lines indicate average values over the 1750-2012 period). Both the discrete and 10 continuous samples experienced identical conditions from ice melt to collection so the reason for offset in 11 measured concentration is likely due to differences in post-processing of the data.



2 Figure S8. Total column air mass back trajectories from the (a) Summit-2010 and (b) Tunu ice core sites over 3 the period 2005-2013 C.E. Maps display the fraction of the total number of trajectory hours (~100000 hrs 4 month<sup>-1</sup>) spent within the total vertical column (under 10000 m). Back trajectories were allowed to travel for 5 10 days. New trajectories were started every 12 hours. Map grid resolution is 2°x2°. Ice core locations are 6 shown by a pink circle. Maps show that air masses consistently arrive at Summit from the SE Greenland coast 7 with a smaller contribution from the SW coast, consistent with the trajectories seen in the boundary layer (Fig. 8 5). Air masses consistently arrive at Tunu from the western Greenland coast with a smaller contribution from 9 the SE.

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Figure S9. Correlation maps of monthly sea ice concentration (SIC) derived from the Summit-2010 ice core. (a) HadISST1 ICE dataset from 1900-2010 C.E. correlated with annual records of MSA. Outliers were removed from the MSA records before the correlations were performed to prevent distortion of the correlations. Month labels indicate the month of SIC compared with the annual MSA value. Only locations that showed a SIC variability greater than 10% and have a significant correlation (t-test, p < 0.05) are displayed. The area of sea ice that is the likely source of MSA (as indicated by the air mass trajectories) are outlined in black [70°- 63°N, 0°- 45°W]. (b) As for (a) but focused on the satellite period 1979-2010 C.E. and the outlined area covers [70°-63°N, 0°-60°W],

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8 Figure S10. Correlation maps of monthly sea ice concentration (SIC) derived from the Tunu ice core. (a)

9 HadISST1 ICE dataset from 1900-2012 C.E. correlated with annual records of MSA. Outliers were removed

10 from the MSA records before the correlations were performed to prevent distortion of the correlations.

11 Month labels indicate the month of SIC compared with the annual MSA value. Only locations that showed a

SIC variability greater than 10% and have a significant correlation (t-test, p<0.05) are displayed. The area of

sea ice that is the likely source of MSA (as indicated by the air mass trajectories) are outlined in black [77 $^{\circ}$ -

 $14~67^{\circ}N,\,62^{\circ}\!-\!50^{\circ}W].$  (b) As for (a) but focused on the satellite period 1979-2012 C.E.





Figure S11. Autocorrelation maps of SIC during (a) the extended era (1900–2012 C.E.) and (b) satellite era (1979–2012 C.E.). Monthly SIC values were compared with the average SIC record from the area which shows the high positive correlation to the Summit-2010 MSA record (outlined in black in Figs. 6a, 6b). There is clearly a negative correlation between sea ice on the east and west coast which is seen over both era from March through to May, but the relationship turns positive in June and July over the extended time period (1900–2012 C.E.)



Figure S12





- 1 Figure S12. Analysis of the effect of errors in the ice core timescales on the correlation between the site MSA
- 2 record and the local sea ice concentrations (SIC). By shifting the dating of the MSA records to either extreme
- 3 of the dating error estimate and replotting the SIC correlation plots (Figs. 6 and 7) it is clear the error in the
- 4 dating of the MSA records does not affect the sign of the correlations displayed on the maps but can have an
- 5 affect on the magnitude of the correlation found in different locations. This is likely a result of the peaks in
- 6 the MSA record being shifted in or out of temporal coherence with peaks in SIC at the different locations.



3 Figure S13: Annual cycle of open water in the ice pack (OWIP) within the aerosol source regions designated

- 4 in Figs. 6 and 7. The annual cycle has been averaged over the period 1900-2012. The satellite period 1979-
- 5 2012 shows the same temporal variability in OWIP at both sites but at reduced OWIP values.
- 6



Figure S14: Summary of the technique used to determine nsiBr: the amount of Bromine in excess of what is expected from a purely sea ice source. (a,b) Blue dots, blue fit line: correlation plots between total bromine and total MSA in Summit-2010 and Tunu ice cores, respectively over the preindustrial period 1750-1880 C.E.. Red dots, yellow fit line: Correlation plots between total bromine and smoothed MSA time series shown in c and d. (c,d) Annual MSA record fit with 9th order polynomial. (e,f) Comparison between the total bromine record (black) and the bromine predicted from the smoothed MSA, Br linear relationship determined in a and b (blue) – the bromine from a purely sea ice source. The difference between the blue and black lines in panels

1 e and f is the amount of bromine in excess of what is expected from a purely sea ice source (nsiBr; see Fig.

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2 8).



Figure S15: Comparison between nitrate and bromine records at both ice core sites. The difference between
the two time-series is most dramatic at the Summit-2010 site because the sea ice record changes most
dramatically at this site – and sea ice is the underlying driver of the bromine record.

#### 1 References

- 2 Legrand, M., Hammer, C., De Angelis, M., Savarino, J., Delmas, R., Clausen, H. and Johnsen, S. J.: Sulfur-
- 3 containing species (methanesulfonate and SO4 ) over the last climatic cycle in the Greenland Ice Core Project
- 4 (central Greenland) ice core, J. Geophys. Res., 102(C12), 26663, doi:10.1029/97JC01436, 1997.
- 5 Mulvaney, R., Pasteur, E. C., Peel, D. A., Saltzman, E. S. and Whung, P.-Y.: The ratio of MSA to non-sea-
- 6 salt sulphate in Antarctic Peninsula ice cores, Tellus B, 44(4), doi:10.3402/tellusb.v44i4.15457, 1992.
- 7 Weller, R.: Postdepositional losses of methane sulfonate, nitrate, and chloride at the European Project for Ice
- 8 Coring in Antarctica deep-drilling site in Dronning Maud Land, Antarctica, J. Geophys. Res., 109(D7), 1–9,
- 9 doi:10.1029/2003JD004189, 2004.

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